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PRESIDENTIAL ADDRESS*

By Dr. Mata Prasad, D.Sc., F.N.I., F.R.I.C.

Ladies and Gentlemen,

It is my extremely sad duty to refer to the untimely and sudden death of Dr. S. S. Bhatnagar, D.Sc., F.R.S., Secretary, Ministry of Natural Resources and Scientific Research, Director, Scientific and Industrial Research, and Chairman, University Grants Commission. We are also informed that it was proposed to appoint him as the Scientific Adviser to the Cabinet. Dr. Bhatnagar was primarily a Chemist, and one of the foremost Chemists in India. His work on the subjects of Colloidal Chemistry and Magnetochemistry ranks high in Physical Chemistry in which he had specialised. His book on Magnetochemistry is the first publication on the subject in English, and is being used as a text-book.

Dr. Bhatnagar also made excellent contributions to the problems of industrial importance and thereby helped to solve the difficult situation which faced our country, particularly during the period of World War II. This work was fully recognised in India and abroad. The Govt. of India conferred on him the O. B. E. in 1936 and Knighthood in 1941, and appointed him as the first Director of the Board and then of the Council of Scientific and Industrial Research. The Attock Oil Company, which was greatly benefited by his work, placed large sums of money at his disposal, which were utilised for awards of scholarships by the Punjab University to research students. The Society of Chemistry and Industry elected him as an Honorary Fellow in 1943, and later, as one of its Vice-Presidents. Universities of Oxford, Patna, Allahabad, Delhi, Banaras, Lucknow, Agra, and Saugor conferred Honorary Doctorate degrees on him.

It will be remembered by senior Fellows of the Society that he was one of the group of three Indian Chemists who endeavoured hard for the establishment of the Indian Chemical Society and took keen interest in the promotion of its welfare. He was also one of the past Presidents of the Society and was twice elected to preside over the deliberations of the Chemistry Section of the Indian Science Congress, the second time being on the occasion of the Jubilee session of the Congress at Calcutta. By his death the Indian Chemical Society and the Indian Chemical world have suffered an irreparable loss.

Through the Council of Scientific and Industrial Research, the organization which was set up by Dr. Bhatnagar, he succeeded in establishing a chain of fourteen National Laboratories in different parts of India, and thus gave a concrete shape to Prime Minister Nehru's vision of the promotion of science in India for the welfare of her people. These laboratories will stand as a lasting memory to his monumental work and will speak volumes for his capacities as the greatest scientific thinker, most skilful organiser, and an able administrator of this age. Let us pray that his historic and unparalleled achieve-

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ments in founding and building up a new era of science in India will bear fruit and make us happy and prosperous.

Many years will pass before India will see his like again.

I take this opportunity to convey my grateful thanks to the Secretary of the Society for the willing co-operation which he and his staff gave me at all times during the tenure of my office. The Secretary is the backbone of every organisation, and its welfare is assured, if he is a sincere and willing worker. In Dr. D. Chakravarti the Indian Chemical Society was fortunate in having a person who has all the qualities of an excellent Secretary. It would seem that the Society will be losing this advantage from this year, since Dr. Chakravarti has now taken up an appointment as the Registrar of the Calcutta University. While congratulating him on his selection to such an elevated position in the University, we are assured by him that he would extend his helping hand and guidance to the Society, whenever required.

One of the eminent Chemists and also one of the three founders and one of the past Presidents of the Society, Dr. J. C. Ghosh, D.Sc., has been appointed as the Vice-Chancellor of the Calcutta University, which is one of the oldest and most advanced Universities in India. We congratulate him on his appointment.

Although the Society is recognised as the Central Organisation of Chemists in India, and is represented in most of the Indian and foreign Assemblies concerned with Chemistry, it is rather distressing to find that in spite of the large increase in the chemical activities in our country, the Fellowship of the Society has not increased to the same extent. The National Register prepared by the Council of Scientific and Industrial Research has the names of 2,767 Chemists, and I am sure there would be many others whose names would appear in the revised edition. To my mind this deficiency is due to the lack of the Branches of the Society. If these Branches are established in all University towns and other places of chemical interest in India, not only the stature of the Society will be enhanced but the Chemists in different parts of the country will be grouped together with bonds of chemical brotherhood. The justification of this suggestion can be realised by looking into the British and American Chemical Societies. Although they have their Central Offices in London and Washington, their activities are resounding through the activities of their Branches in all corners of the U.K. and U.S. I do not claim any originality for this idea, for I clearly remember that it was there in the minds of the three musketeers when in 1926 they asked me to start a Branch of the Society in Bombay, this being the only Branch in India which has worked satisfactorily for the last 29 years. I congratulate the Fellow Chemists of the Bombay Branch on their remarkable work and solicit the co-operation of all the Fellows of the Society in establishing other Branches of the Society with the same zeal as in Bombay. I also request our President-Elect, Dr. B. C. Guha, to give due consideration to this proposal.

Soap Gels in Aqueous and Non-aqueous Media

Ladies and Gentlemen, the subject which I have chosen for my address deals with the study of gels in which the workers of the Institute of Science, Bombay, have been interested for some time.

Late Prof. McBain (the first Director of the National Chemical Laboratory of India, Poona) and co-workers[1] were the pioneers in the field of study of soap gels in aqueous medium. Their work has shown that, excepting at very high dilutions, aqueous systems of soap are colloidal in nature, having highly charged and heavily hydrated ionic micelles, the mobility of which is of the same order of magnitude as that of an ordinary ion. This peculiarity of soap solutions led Prof. McBain to give soaps the special name of "colloidal electrolytes". The behaviour of soaps as colloidal electrolytes, deduced mainly from the measurement of the electrical conductivities of their aqueous solutions, has been confirmed by McBain and co-workers[1] from the results of freezing point, vapour pressure, osmotic activity and migration experiments. McBain has also postulated the existence of micelles of different kinds, sizes, shapes and compositions in soap solutions. The sizes of these micelles have been found to be a few times bigger than those of the soap molecules.

McBain and his co-workers have also shown that an aqueous solution of sodium oleate can be brought into any of the three typically colloidal states, namely, clear oily liquid sol, white opaque solid, curd and clear transparent elastic gel. They have shown from measurements of refractive indices of the soap in the three states that the soap particles in the sol and the gel states are identical.

1. Solubility of Soaps and Phase Changes in their Solutions

McBain and co-workers[2] have studied intensively, by specical techniques developed by them, solubilities of soaps and the changes in phase undergone by the anhydrous and hydrated soaps when heated to high temperatures with or without the addition of water and some organic solvents with a view to elucidating the behaviour of soaps on dispersion in different media. For example, they have determined the behaviour of anhydrous sodium palmitate in nineteen different organic solvents over the whole range of temperature and composition, and found that although the soap is miscible in all proportions in all solvents at suitably high temperatures, it undergoes various phase changes as the systems are cooled to lower temperatures.

The appearance of different phases above and below the solubility curves has been fully described by these authors ; the sharp elbows occurring in the solubility curves have been attributed to the formation of colloidal micelles. Vold and co-workers[3], Lawrence[4] and others have also investigated the solubility and phase changes undergone by alkali soaps in aqueous and non-aqueous media, and have observed as many as eleven different phases of soaps, namely, isotropic liquid, neat soap, waxy soap, sub-waxy soap,plastic soap, soap curds, anisotropic gels, isotropic gels and other intermediate states.

Recently some work has been done on the phase changes undergone by sodium soaps in Nujol, alcohols and glycerine[5] at Bombay and several phases have been observed in these systems as well; these results have been suitably interpreted to elucidate the structure of soap gels in these solvents.

2. Preparation of Soap Gels in Non-aqueous Media

It will be observed from the above account that in most cases higher temperatures are necessary to bring about complete solution of soaps in non-polar than in polar solvents. Important factors which affect the solubility of soaps in different solvents are: (*i*) the nature, number and space relationships of the polar groups of the solvent molecules, (*ii*) the polarity of the solvents as measured by the quotient of displacement and molar volumes, and (*iii*) the size and shape of the solvent molecules. Soap gels have therefore been prepared by several investigators, particularly by Fischer and co-workers[6], McBain and collaborators[7], Da Fano[8], Lawrence[9], and Prasad and co-workers[10] in a large number of non-aqueous solvents, such as alcohols, hydrocarbons, mineral oils and others, in which soaps are generally only sparingly soluble in the cold, but they go into solution or get dispersed on heating the soap-solvent mixture to a high temperature, which in most cases approaches the boiling point of the solvent. On cooling, these systems set to gels, if the concentration of the soap in the solution falls within a certain range, depending upon the solvent.

3. Cooling Curves of Soap-solvent Systems

Since the soap gels in non-aqueous solvents are prepared by cooling hot solutions of soaps in solvents, several investigations have been carried out on the cooling curves of these systems. They have revealed that in all cases heat is evolved during gelation. The heating curves of these systems have shown that the thermal conductivity is generally less in the sol than in the gel states.

4. Process of Formation of Soap Gels in Non-aqueous Media

The process of gel formation and the determination of the structure of gel form a very interesting study. The formation of a soap gel or, as a matter of fact, of a gel of any substance is considered to take place in three stages. The first stage consists in bringing the gel-forming substance in the sol state. For this purpose an important condition is that a sufficient amount of the gel-forming substance should be obtained in a supersaturated state. The importance of this condition has been deduced from the experimental fact that under given conditions certain concentration limits are prescribed for the formation of each gel. The extensive investigations conducted by Von Weimarn[11] have also established that gel formation takes place only when the factors involving viscosity and the degree of supersaturation are large and the solubility of the gel-forming substance is small.

The second stage in gelation consists in the coalescence or aggregation of the particles of the sol. This process of agglomeration is accompanied by a very strong attachment of the surrounding (dispersion) medium on account of which the particles get heavily "solvated".

The third stage in gelation corresponds to the formation of specific structures which are fairly complicated. During this process complete immobilisation of the dispersion medium takes place. The viscosity and the surface tension of gel-forming systems also increase rapidly at this stage.

5. Theories of Gel Structure

Various theories have been put forward regarding the structure of gels. Of these, the most important are those which consider the gel as a liquid-solid (two phase) system. They are (*i*) the cellular theory and (*ii*) the fibrillar theory.

According to the cellular theory, the structure of gels is made up of cells, built of the solid phase, which hang together at certain points to form a network. The liquid phase of the gel is held in the form of droplets inside the cellular framework. The fibrillar theory assumes that gels are made up of fibrous structures formed of the solvated solid phase, and the liquid phase is contained in the pores of these fibres or aggregates, both phases being continuous. The fibrils may be formed by mechanical agglomeration of the colloid or may consist of very large polymerised molecules of micelles of the gel-forming substance.

The cellular theory has been supported by the ultra-microscopic observation of structures of silica gels by Bütschli[12]. This theory accounts for the elasticity of gels, but cannot explain satisfactorily the phenomena of swelling, dehydration, diffusion and syneresis. These are better explained on the basis of the fibrillar theory which also accounts for the elasticity of gels Actually, Poole[13] has shown that the values obtained for the elasticity of gelatin and cellulose acetate gels agree in a qualitative and in an approximately quantitative manner with the theoretical values calculated on the assumption that the gel sturcture consists of a mesh of cylindrical fibres. The regularity of changes in the physical properties observed during the sol gel transformation in various systems also support the fibrillar theory.

The validity of the fibrillar theory of gel structure has been supported by McBain and by Prasad[14] for soap gels as well. Their conclusions are based upon the study of the several properties and distinguishing behaviour of soap gels.

6. Caracteristics of Soap Gel-forming Systems

An account of several characteristics of soap gel-forming systems studied during and after gelation is given in the following pages.

(*a*) *Time and Temperature of Setting*

The setting of a gel has been defined by different criteria, but all of them, with the exception of Prasad and Hattiangdi's optical method[15], are based on the attainment of a certain viscosity by the gel-forming mixture. The time taken by a mixture to attain a particular value of viscosity is taken as the time of setting which is considered as a characteristic property of the gel. Several methods in vogue for this measurement are due to Fleming[16], Fells and Firth[17], Hurd and Letteron[18], Trotman and Ball[19], Friedman and Shearer[20], Reiger[21], and Dharmatti and Hattiangdi[22], and have been used in case of inorganic gels and organic gels in which the sol-gel transformation is isothermal.

Fleming's method is most convenient for the study of time of setting of soap gels in non-aqueous media, and hence it has been employed by Prasad and co-workers[23]

for a systematic study of this property. It has been found that an increase in the soap content of gel-forming systems decreases their time of setting. In case of soap gels in alcohols, the time of setting has been found to increase as the series of alcohols is ascended; this may be due to the constitutive properties of the solvents used.

A significant observation has been made that the time of setting decreases when the temperature of the surroundings is lowered, indicating thereby that the time of setting decreases as the rate of cooling is increased. This observation has been confirmed by measuring the time of setting of a system containing the same amount of soap in the same amount of the solvent under various conditions which alter the rate of cooling. Hence it has been concluded that the time of setting cannot be taken as the fundamental or the characteristic property of gels formed by cooling a gel-forming system.

Deshpande and Buch[24] have observed that the temperature of setting, defined as the highest temperature at which a soap gel-forming solution sets to a gel, of a particular gel-forming system is independent of the rate of cooling. Hence they have concluded that temperature and not time of setting is the characteristic property of such gels. The temperature of setting or gelation temperature, however, increases as the concentration of soap is increased. Further, they have shown that the observed time of setting is approximately the same (a little higher) as the time, calculated from the cooling curves, required for a gel-forming system to cool from the temperature of setting to the surrounding temperature. The slight difference between the two values is due to the heat evolved during gelation. A gel-forming system would not set to a gel if the temperature to which it is cooled is higher than the gelation temperature.

(*b*) *Elasticity and Gel-strength*

Elasticity is another important property of the gel state. The importance of this property was recognised even in the early days, but its significance in elucidating the structure of gels has been understood only recently. Most of the work on the elasticity of gels has been conducted on gels of gelatin by Shepperd and co-workers[25], Lampitt and co-workers[26] and Hatschek[27]. Some data have also been obtained on the elasticity of gels of cellulose acetate by Mardles[28]. However, an exhaustive and systematic investigation on the elasticity of cellulose acetate gels in benzyl alcohol has been carried out by Poole[29], who introduced a term, coefficient of "inner resistance", to denote the force required to produce unit velocity of "creep", the increase in the deformation with time when a steady stress is applied to a unit area of the gel in the absence of all elastic controlling forces.

The gel strength of sodium oleate gels in pinene has been studied by Prasad and co-workers[30], who along with other workers have shown that the gel-strength varies directly as the square of the concentration of the gel-forming substance.

(*c*) *Diffusion*

The rate of diffusion of solutions of simple substances in dilute gels has been found to be similar to that in pure liquids. However, in general, substances of high mole-

cular weights diffuse very slowly in gels, while for colloidally dispersed substances the gels serve as filters, as they allow only the dispersion medium to pass through. The diffusion in gels of gelatin and agar-agar has been extensively studied by several workers. It has been generally observed that the rate of diffusion of a substance decreases with an increase in the concentration of the gel and is influenced by the presence of other substances. Watanabe[31] has deduced an empirical relation,

$$d/t = m\log c + n,$$

between the concentration (c) of the diffusing substance and the rate of diffusion (d/t). Friedman and co-workers[32] have used Weaver's theory[33] to deduce a relation for the rate of diffusion in water and in a gel; this involves the radius of the diffusing molecule and the average radius of the pores in the gel. All the aforesaid investigations refer to gels in water. Friedman and Klemm[32] and Adarkar[34] have respectively found that the laws of diffusion are also applicable to the diffusion in cellulose acetate gels in benzene and soap gels in alcohols.

(*d*) *Syneresis and Desorption*

An interesting and important property exhibited by some gels is that they on standing exude spontaneously the liquid contained in them. This phenomenon was first observed by Graham[35] who called it as "syneresis". Ostwald[36] has pointed out that syneresis is not a characteristic of gels of particular substances as it is exhibited by gels of several substances differing widely from each other in their properties. The liquid exuded in most cases is a saturated solution of the dispersed phase in the dispersion medium. Holmes and co-workers[37], Lipatov[38], Mukoyama[39], Ferguson and Applebey[40], Bonnel[41], Prakash and Dhar[42] and others have quantitatively studied the velocity of syneresis, using different methods for the measurement of the liquid exuded.

Prasad and co-workers[43, 44] have systematically and exhaustively studied the influence of various factors, such as the surface, the concentration of the gel-forming substance, the temperature at which the gel is allowed to synerise, the volume of the gel-forming substances on the syneresis of sodium soaps in organic solvents and their mixtures. It is concluded that the progress of syneresis does not follow the relation for the reaction of first order, but corresponds to the relation for the imbibition of liquids taking place in two stages, the syneresis in the second stage being much slower than in the first.

As against syneresis, which is a spontaneous process, the liquid contained in a gel can be removed also by drying or desorption. The first important investigation on the drying of gels was conducted by Van Bemmelen[45] on silicic acid gels. This work, which was extended by Zsigmondy and Anderson[46], has led to the important conclusion that (*i*) the relationship between water content of the gel and relative vapour pressure is not reversible, (*ii*) the rate of dehydration depends on the previous history of the gel and (*iii*) when dried to extreme limits, the contraction of the gel is accompanied with changes in opacity. Desorption of a soap (sodium stearate) gel in a non-aqueous medium (pinene) was investigated for the first time by Hattiangdi[47] who found that the rate

of desorption decreased with increase in the soap content of the gels, and that the process of desorption was a surface phenomenon.

(e) *Viscosity*

Another important study in connection with gels is the determination of the change in the viscosity of gel-forming systems during sol-gel transformation. The subject has assumed great importance, not only because viscosity can be measured quantitatively by relatively simple methods, but also because viscosity correctly indicates the changes that take place in a colloidal system during coagulation and gelation. Hence Graham[48] called viscometer a colloidoscope.

Most investigations reported in the literature deal with gel-forming systems of inorganic substances. However, Von Schroeder[49], Levite[50], Sheppard[51] and Banerji and Ghosh[52] have studied the changes in viscosity during gelation of gelatin gels under various conditions and have concluded that for some time the rate of increase of viscosity is nearly proportional to the time, but afterwards it becomes irregular. However, Shoji[53] has shown that viscosity variations during the gelation of gelatin solution are given by $\eta - \eta_1 = \mu t / (1 + \mu t/\lambda)$.

Prominent contribution to the viscometric study during the sol-gel transformation of gel-forming systems in non-aqueous media has been made by Mardles[54] in the case of cellulose acetate dispersed in benzyl alcohol. He found that the initial regularities in the viscosity-time curves could be empirically expressed as $\eta - \eta_0 = ae^{Kt}$. Arisz[55] has obtained sigmoid curves for the viscosity changes taking place in solutions of gelatin in glycerine with time.

Prasad and co-workers[56] are the pioneers in the field of the study of the viscosity changes taking place in soap gel-forming systems in organic media. They have concluded that (*i*) Einstein's equation $\eta = \eta_0 (1 + K\rho)$, where ρ is the concentration of the solution, is obeyed by these systems at and above 100°, showing thereby that they are true molecular solutions, and (*ii*) at lower temperatures, the viscosity changes are rapid till the systems set to gels. Recently, the viscosity changes during and after gelation of sodium oleate-Nujol systems of different concentrations have been recorded[57] with respect to the changes in temperature taking place in the gel-forming solutions during cooling. The conclusions drawn from this study are similar to those obtained by previous workers (cf. Prasad and co-workers). On plotting the values of log η against $1/T$, ($T = 273 + t°C$), it is found that the plotted points lie approximately on straight lines, indicating a relation of the type $\eta = Ae^{-B/T}$, where A and B are constants. It has been concluded from this study that the system of sodium oleate in Nujol is akin to an "isogel". The very steep rise in viscosity observed during the last stage of gelation is ascribed to the formation of a structure similar to that of a solid, which offers large resistance to flow.

(f) *Optical Properties*

Till now we have been dealing with properties of gel-forming systems in the measurement of which these systems are continually disturbed. The study of the optical

properties has a distinct advantage in that the gel system is not at all disturbed. The optical properties generally studied are the opacity, extinction coefficient, turbidity and scattering of light.

The measurement of opacity changes during gelation gives an idea of the changes taking place in size and number of the particles of gel-forming systems during and after gelation. Although changes in opacity during the gelation of several inorganic gels were studied by various workers, these were first studied in the case of sodium oleate gels in pinene. Hattiangdi[58] has observed that the opacity-time curves are generally S-shaped, but those for low soap-content show a distinct change in direction after the S-shaped stage is reached. The opacity-temperature curves have also been found to show a similar behaviour. Recently Sundaram[59] has studied the opacity changes during the syneresis of sodium oleate gels in pinene and has observed that both opacity changes and syneresis are due to the same structural changes taking place in the gels.

In recent years, increasing attention is being paid to the study of the scattering of light by solutions of high polymer molecules and by colloidal systems. This is due to the fact that both the shape and size of the particles can be judged from the measurement of the scattered light. In fact, the size can be estimated in a quantitative manner and according to Debye[60], the weight-average molecular weight of polymers in solution can be evaluated from a knowledge of the intensity of scattered light and the refractive index of the solution.

Formerly, the changes taking place in the intensity and the depolarisation factor (ρ_u) of the light transversely scattered, using incident light unpolarised, were measured to follow the changes taking place in the size of the particles (cf. Krishnamurti[61]). The intensity of the transversely scattered light was split up into density and anisotropic scatterings, using the relation,

$$I_D = I_{90} \times \frac{6 - 7\rho_u}{6 + 6\rho_u} \text{ and } I_A = I_{90} - I_D = I_{90} \times \frac{13\,\rho_u}{6 + 6\rho_u}.$$

Later, Krishnan[62] pointed out that it was also necessary to measure the depolarisation factors ρ_v and ρ_h, using the incident light polarised vertically and horizontally, respectively. Krishnan[63] has shown that variations in ρ_v values indicate variations in the anisotropy (deviations from spherical shape) of the particles-(the ρ_v value of the light transversely scattered by a spherical particle being zero), and that the variations in the value of ρ_h of the transversely scattered light indicate the changes in the size of the particle compared to the wave-length of light. It has also been shown that the value of ρ_u is related to those of ρ_v and ρ_h by the relation,

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v).$$

From this it has been deduced that changes in the values of

$$\Delta\rho_u = \rho_u - \frac{2\,\rho_v}{1 + \rho_v}$$

indicate to a first approximation the changes in the size of the particles[64]. These

measurements have been carried out on a number of inorganic gel-forming systems by Ramaiah[65], Katti[66] and Prasad and co-workers[67].

Rayleigh's simple equation[68] for the angular distribution of intensity of scattered light was not found to explain the distribution of intensity of light scattered by large particles. A new theory of the "optics of turbid media" was developed by Mie[69]; this theory had been extended by Shoulejkin[70], Blumer[71], Krishnan[72], Gans[73] and recently by LaMer and co-workers[74] to many different systems. Their investigations show that in the case of scattering by large particles, the angular distribution of intensity is not symmetrical about the transverse direction. As the size of the particle increases, the intensity of light scattered in the forward direction increases more rapidly than that in the backward direction and for very large particles the intensity distribution is of an oscillatory nature. Debye, Oster, Mark, Zimm, Doty, and their co-workers[75] have shown that the ratio of the intensity of light scattered at any angle in the forward direction to that scattered at an angle in the backward direction, situated symmetrically about the transverse direction, is a characteristic (quantity) of the particular polymer solution. Generally the ratio $I_{45°}/I_{135°}$ or $I_{50°}/I_{130°}$ is measured and is called the "dissymmetry" of the polymer solution. These investigators have shown that for any given polymer solution, the ratio depends upon the concentration of the polymer and on the size, that is, the weight-average molecular weight of the polymer. This ratio has been found to increase with size (compared to wave-length) in a definite manner for molecules of rod shape, of spherical shape, and of a random coil type.

Recently the depolarisation factors[76] and the angular variation of the intensity[77] of light scattered from gel-forming systems of sodium soaps in organic solvents have been investigated. A difference has been observed in these values when the soaps are dispersed in polar and in non-polar solvents. This difference has been explained on the nature of orientation of soap molecules in polar solvents. The results show that in soap gels in xylene the particles are highly anisotropic and also of appreciable size. However, in the case of gels in alcohols, it has been observed that the final particles are less anisotropic and probably of a smaller linear dimension than the initial ones. This difference has been explained on the nature of orientation of soap molecules in polar solvents.

Although Marton, McBain and Vold[78] have observed ribbon like curd fibres by electron microscopic examination of sodium laurate film, Vold, Coffer and Baker[79] have shown by electron microscope photographs of slices of gels of metallic soaps in hydrocarbons that there are no definite soap fibres in the system but only discrete agglomerates of irregularly shaped particles are present. These pictures also show that the gels contain secondary mesh-like soap particles and that quenched gels (that is, gels formed by rapid cooling) have more regular mesh-like structure than the slowly cooled gels. So far X-rays and electron microscope have not been extensively applied for the investigation of structure of soap gels so as to lead us to definite conclusions. Let us hope that in near future these modern tools of science will be applied freely to unravel the mystery of the structure of soap and other gels.

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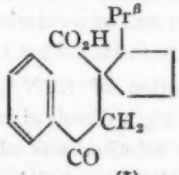
STUDIES IN CATALYTIC DEHYDROGENATION. PART VI

By Suresh Chandra Sen Gupta* and Dhirendra Nath Chatterjee

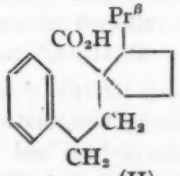
The synthesis and catalytic dehydrogenation of 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(2′-*iso*propyl*cyclo*pentane) have been effected. This spiran on dehydrogenation with Pt—C catalyst furnishes 1-methylpyrene only.

In Parts IV and V of this series (this *Journal*, 1954, **31**, 285, 911) it had been shown that spirans containing an ethyl substituent in 2′-position of the spiro-*cyclo*pentane ring as in 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(2′-ethyl*cyclo*pentane) (IV, Et in place of Pr^{β}) gave on catalytic dehydrogenation a pyrene derivative. A probable mechanism of ring transformation was postulated there. The validity of this mechanism of ring transformation has now been further supported by the observation that the spiran 1:2:3:4-tetrahydronaphthalene-2 : 2-spiro-(2′-*iso*propyl*cyclo*pentane) (IV) furnishes on catalytic dehydrogenation a good yield of 1-methylpyrene (VI) only. According to our view of the mechanism of the ring transformation, the formation of 1-methylpyrene can be explained here on the assumption that the *cyclo*pentane ring undergoes fission near the heavy *iso*propyl group (along the dotted lines) with the formation of an intermediate which by angular cyclisation forms a partially reduced 4-*iso*propylphenanthrene. This *iso*propyl group in C_4-position of the phenanthrene ring facilitates the formation of a new 6-carbon ring by cyclodehydrogenation through linkage with C_5 affording ultimately 1-methylpyrene. In order to lend further support to our view on the course of the reaction, an attempt was made to synthesise 4-*iso*propylphenanthrene by the action of *iso*propylmagnesium iodide on 4-keto-1:2:3:4-tetrahydrophenanthrene, but it failed as *iso*propylmagnesium iodide did not condense with the ketone.

The spiran (IV) has been synthesised by an extension of the method followed in Part I of this series (this *Journal*, 1952, **29**, 438). The anhydride of 2-*iso*propyl*cyclo*pentane-1-carboxy-1-acetic acid condensed with benzene in presence of anhydrous aluminium chloride yielding a single keto-acid which had been proved to be αα-(2′-*iso*propyl*cyclo*pentane)-β-benzoylpropionic acid (I). This keto-acid reacts with salicyl aldehyde affording a pyrylium salt, thus showing the presence of a $-CH_2-CO-$ grouping (Desai and Wali, *Proc. Ind. Acad. Sci.*, 1937, **6A**, 135), while on reduction it furnishes αα-(2′-*iso*propyl*cyclo*pentane)-γ-phenylbutyric acid (II). This on cyclisation with 85% sulphuric acid at 100° gives a good yield of 1-keto-1 : 2:3:4-tetrahydronaphthalene-2 : 2-spiro-(2′-*iso*propyl*cyclo*pentane) (III). This cyclic ketone on reduction by the Clemmensen method furnishes the desired spiran (IV).



(I)



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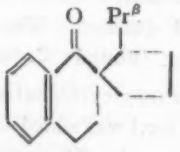

(III)

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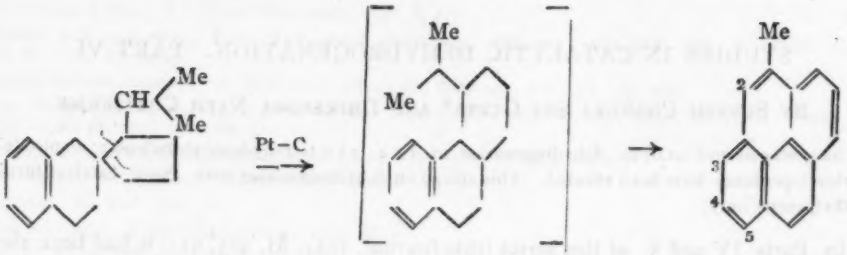

(IV) (V) (VI)

EXPERIMENTAL

2-*iso*Propyl*cyclo*pentane-1-carboxy-1-acetic acid required for the above synthesis was prepared from 2-*iso*propyl*cyclo*pentanone and ethyl cyanoacetate according to the method of Lapworth and McRae (*J. Chem. Soc.*, 1922, **123**, 2754) and Cope (*J. Amer. Chem. Soc.*, 1941, **63**, 3452).

2-iso*Prophyl*cyclo*pentanone*.—2-Carbethoxy*cyclo*pentanone (62 g.) was added slowly to powdered potassium (16 g.) in dry benzene (400 c.c.), cooled in ice. It was kept at room temperature for 12 hours and then heated on a water-bath for 36 hours after addition of *iso*propyl iodide (45 c.c.). The product was decomposed with ice-cold water and the separated benzene layer was washed with water, dried and the benzene distilled off. 2-*iso*Propyl-2-carbethoxy*cyclo*pentanone distilled at 95°-97°/2 mm. as a colorless liquid, yield 58 g. (Found: C, 66.4; H, 9.2. $C_{11}H_{18}O_3$ requires C, 66.6; H, 9.1 per cent). The *iso*propylated keto-ester was boiled with HCl (1:1, 500 c.c.) for 24 hours. The product was saturated with ammonium sulphate and thoroughly extracted with ether. The ether extract was washed with cold water, dried with anhydrous K_2CO_3 and the ether removed with a good fractionating column. 2-*iso*Propyl*cyclo*pentanone came over at 172°-174° as a colorless liquid, yield 30 g. It readily formed semicarbazone which crystallised from alcohol in needles, m.p. 193°. (Found: C, 58.8; H, 9.4. $C_9H_{17}ON_3$ requires C, 59.0; H, 9.3 per cent). The ketone had been prepared by Kötz and Schüler (*Annalen*, 1906, **350**, 227).

Ethyl 2-iso*Propyl*cyclo*pentylidene-cyanoacetate*.—A mixture of 2-*iso*propyl*cyclo*pentanone (30 g.), ethyl cyanoacetate (27 g.), acetic acid (29 c.c.), ammonium acetate (9.2 g.) and benzene (120 c.c.) was heated in an oil-bath in a Cope's apparatus at 130°-140° for 6 hours and then at 140°-150° for 12 hours when separation of water was complete. The unsaturated nitrile was extracted with a little fresh benzene, washed with water, dried and distilled. The product collected at 120°-122°/3 mm. as a colorless liquid, yield 42 g. (Found: C, 70.4; H, 8.5. $C_{13}H_{19}O_2N$ requires C, 70.6; H, 8.6 per cent).

2-iso*Propylcyclopentane-1-carboxy-1-acetic Acid*.—A solution of KCN (30 g.) in water (62 c.c.) was added to the foregoing unsaturated nitrile (42 g.), dissolved in rectified spirit (220 c.c.). There was evolution of heat and the clear solution was allowed to stand for a week. Alcohol was then distilled off and the dark semisolid mass was boiled under reflux with HCl (conc., 500 c.c.) for 42 hours. The separated acid

was extracted with hot sodium carbonate solution (charcoal) and precipitated with HCl (conc.). The dicarboxylic acid crystallised from dilute HCl in plates, m.p. 164-65°, yield 26 g. (Found : C, 61.56 ; H, 8.3. $C_{11}H_{16}O_4$ requires C, 61.68 ; H, 8.4 per cent).

The *anhydride* was obtained by heating the acid with acetic anhydride for 6 hours. It had b.p. 135-36°/3 mm. (Found : C, 67.2 ; H, 8.3. $C_{11}H_{14}O_3$ requires C, 67.3; H, 8.16 per cent). The *anilic acid* was prepared by heating the anhydride with aniline in benzene solution. It crystallised from rectified spirit in fine needles, m.p. 147°. (Found : C, 70.4 ; H, 8.0. $C_{17}H_{23}O_3N$ requires C, 70.6 ; H, 7.9 per cent).

αα-(2′-isoPropylcyclopentane)-β-benzoylpropionic Acid (I).—Powdered $AlCl_3$ (28 g.) was gradually added to a solution of the anhydride of the preceding acid (20 g.) in dry benzene (60 c.c.), cooled in ice. It was kept at the ordinary temperature for 12 hours and then heated at 60°-70° for 3 hours when evolution of HCl ceased. It was then decomposed with ice and HCl and benzene was distilled off in steam. The crude keto-acid was dissolved in hot sodium carbonate solution and was precipitated with hydrochloric acid. The semisolid mass, thus obtained, was triturated with little petroleum ether (b.p. 40°-60°) when it completely solidified. It was twice crystallised from benzene-hexane mixture when it was obtained in stout colorless needles, m.p. 115°, yield 12 g. (Found : C, 74.3; H, 8.1. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.0 per cent).

The *semicarbazone* of the keto-acid (I) was obtained when the keto-acid was heated with semicarbazide acetate in alcoholic solution for 6 hours. The semisolid semicarbazone left after removal of alcohol solidified on trituration with petroleum ether. It separated from alcohol in short needles, m.p. 172-73° (decomp.). (Found: C, 65.1; H, 7.6. $C_{18}H_{25}O_3N_3$ requires C, 65.3; H, 7.5 per cent).

Pyrylium salt of the Keto-acid.—A mixture of the keto-acid (0.1 g.) and salicyl aldehyde (0.1 g.) in absolute ethyl alcohol (10 c.c.) was saturated with dry HCl gas at 0° and kept in the ice chest for 3 days when dark red pyrylium salt separated. It was soluble in alkali and did not melt up to 290°.

αα-(2′-isoPropylcyclopentane)-γ-phenylbutyric Acid (II).—The foregoing keto-acid (8 g.) was gently boiled under reflux with amalgamated zinc (32 g.) and HCl (conc., 32 c.c.) for 24 hours. The product was extracted with ether, washed with water and the solvent removed. The residual oil was dissolved in hot sodium carbonate solution. The reduced acid that separated on acidification of the alkaline filtrate was taken up in ether and after removal of the solvent was distilled under reduced pressure. The butyric acid came over at 180°-185°/3 mm. as a viscous colorless liquid, yield 5 g. (Found : C, 78.1; H, 9.2. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.2 per cent).

1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(2′-isopropylcyclopentane) (III).—The foregoing butyric acid (6 g.) was mixed with H_2SO_4 (conc., 18 c.c.) and water (6 c.c.) and was heated on the water-bath for 1½ hours with stirring. After decomposition with ice the spiro-ketone was taken up in ether. The ethereal solution was washed with ammonia, and then with water, dried and the solvent removed. The ketone distilled at 170°-172°/6 mm. as a colorless liquid with a characteristic odour, yield 3.5 g. (Found : C, 84.15; H, 9.02. $C_{17}H_{22}O$ requires C, 84.3; H, 9.1 per cent).

1½2:3:4-Tetrahydronaphthalene-2:2-spiro-(2′-isopropylcyclopentane) (IV).—The spiro-ketone (III, 3 g.) was gently boiled with amalgamated zinc (15 g.) and HCl (conc.,

15 c.c.) for 24 hours with occasional addition of HCl (6 c.c.) after every 6 hours. After dilution with water the product was taken up in ether. The ether extract was washed with water, dried and the solvent removed. The spiro-hydrocarbon came over at 152°-155°/5 mm. as a colorless mobile oil, yield 2 g. (Found: C, 89.2; H, 10.3. $C_{17}H_{24}$ requires C, 89.5; H, 10.5 per cent).

Dehydrogenation of 1 : 2 : 3 : 4-*Tetrahydronaphthalene*-2 : 2-*spiro*-(2′-*isopropylcyclopentane*) (IV) *with* Pt-C *catalyst*.—The spiro-hydrocarbon (3 g.) was heated with Pt–C catalyst (0.3 g.) in a metal bath at 290°-300° for 6 hours. The temperature was then gradually raised from 300°-330° in course of 6 hours when no further hydrogen was evolved. The dehydrogenation product was thoroughly extracted with ether-benzene mixture and the residual oil left after removal of the solvent was distilled over sodium under reduced pressure. The liquid distillate (1.5 g.) was warmed with an alcoholic solution of picric acid (1.5 g.). The separated *picrate* after one crystallisation from absolute alcohol was obtained as beautiful red needles melting at 227°. (Found: C, 61.9; H, 3.42. $C_{23}H_{15}O_7N_3$ requires C, 62.0; H, 3.4 per cent).

The picrate was decomposed with aqueous ammonia and the liberated hydrocarbon was taken up in ether. The ether solution was washed with water and the solvent removed. The solid *hydrocarbon* left after removal of the ether crystallised from methyl alcohol in colorless flakes, m.p. 147°. The mixed m.p. of this sample with an authentic sample of pyrene was depressed. (Found: C, 94.4; H, 5.6. $C_{17}H_{12}$ requires C, 94.44; H, 5.56 per cent).

Bachmann and Edgerton (*J. Amer. Chem. Soc.*, 1940, **62**, 2970) record m.p. of 1-methylpyrene as 147.5°–148.5° and that of its picrate as 226-27°. The sym-*trinitrobenzene complex* was prepared with the hydrocarbon in alcoholic solution. After crystallisation from absolute alcohol it was obtained as orange needles melting at 246-47° (Found: C, 64 4; H, 3.55. $C_{23}H_{15}O_6N_3$ requires C, 64.3; H, 3.5 per cent).

The hydrocarbon responded to the colour reaction shown by Bachmann and Edgerton (*loc. cit.*) in case of 1-methylpyrene. It gave a golden yellow solution with H_2SO_4 (conc.) having a green fluorescence. On gentle warming the colour became olive-green with intense violet fluorescence.

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*iso*QUINOLINE DERIVATIVES. PART I

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Bischler-Napieralski cyclisation of (α-acetamido-β-phenyl)-ethylmethyl ketone and of the corresponding *p*-nitro analogue with phosphorus oxychloride in presence of nitrobenzene furnishes 1-methyl-*iso*quinoline and 1-methyl-7-nitro*iso*quinoline (VI) respectively, the process involving cyclisation, dehydrogenation and deacetylation (cf. Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2962). The exact sequence of the three processes involved is not clear. (VI) can also be obtained by using concentrated sulphuric acid as the cyclising agent. The intermediate compounds prepared in course of this investigation are represented by (I), (II), (III), (IV) and (V).

In view of the observation that methyl*iso*quinolines exhibit spasmolytic property with low toxicity (Kreitmair, *Arch. exp. Path. Pharm.*, 1932, **164**, 509; B. P. 488,423; Sugasawa and Sugimito, *J. Pharm. Soc. Japan*, 1941, **61**, 62; Polgar and Zelenka, *Magar Nogyoyaszok Lapja*, 1948, **7**, 1) and that the activity is enhanced by introduction of basic groups into methyl*iso*quinolines (cf. Merck, D. R. P. 549,967), it has been considered to be of interest to synthesise 3:4-dihydro*iso*quinolines having a methyl group at the 1-position and a strong basic group at the 3. The significance of the suggestion regarding a 3:4-dihydro derivative has been emphasised by the observation on the interesting physiological activity of 3- or 4-methyl-3:4-dihydro*iso*quinolines (Sommers and Weston, *J. Amer. Chem. Soc.*, 1951, **73**, 5749).

In an approach to the synthesis of a 3:4-dihydro*iso*quinoline with a strong basic group attached to the 3-position, it has been planned to prepare a derivative of 3-acetyl-3:4-dihydro*iso*quinoline, so that the latter can be subjected to the Mannich reaction to afford the desired product. Clemo and Popli (*J. Chem. Soc.*, 1951, 1406) have recently prepared 3-acetyl*iso*quinoline by condensing ethyl *iso*quinoline-3-carboxylate with ethyl acetate in presence of potassium ethoxide in toluene and by hydrolysis of the corresponding β-keto-ester and subsequent decarboxylation. Padbury and Lindwall (*J. Amer. Chem. Soc.*, 1945, **67**, 1268) prepared previously 1-acetyl- and 4-acetyl-*iso*quinolines by a similar reaction under the Claisen condition. However, the synthesis of a 3-acetyl-3:4-dihydro*iso*quinoline derivative does not appear to have been so far described. In view of the observation by Clemo and Popli (*loc. cit.*) that condensation of ethyl 1:2:3:4-tetrahydro*iso*quinoline-3-carboxylate with ethyl acetate under the Claisen condition gives poor yield of the product, some other route to prepare a 3-acetyl-3:4-dihydro*iso*quinoline derivative has now been attempted. Preliminary experiments to this end have now involved hydrolysis of ethyl α-carbethoxy-α-acetamido-β-phenylpropionate (Snyder, Shekleton and Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 310) with one equivalent of potassium hydroxide (cf. Albertson *et al.*, *ibid.*, 1948, **70**, 1150) to its half-ester α-carbethoxy-α-acetamido-β-phenylpropionic acid, isolated as a heavy liquid. This crude half-ester has been next subjected to the Dakin and West reaction (*J. Biol. Chem.*, 1928, **78**, 91, 745, 757; cf. Albertson *et al.*, *loc. cit.*) with acetic anhydride in presence of pyridine, so that the corresponding ketone, if obtained, may

be converted by the Bischler-Napieralski cyclisation into a 3 : 4-dihydro*iso*quinoline derivative having an acetyl group in the 3-position. But in this Dakin and West reaction an intractable tarry matter has been obtained, from which no pure substance could be isolated.

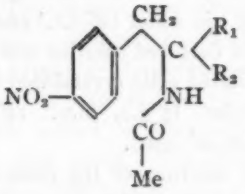
The next approach consists in condensation of *p*-nitrobenzyl chloride with ethyl acetamidomalonate to yield ethyl α-carbethoxy-α-acetamido-β-*p*-nitrophenylpropionate (I) (cf. Albertson and Archer, *J. Amer. Chem. Soc.*, 1945, **67**, 308). By hydrolysis of (I) with alkali and subsequent decarboxylation of the corresponding dicarboxylic acid (II) in presence of boiling water, it has been possible to prepare α-acetamido-β-*p*-nitrophenylpropionic acid (III). That during such hydrolysis of (I) to (II) the acetyl group has not been split off is supported by the observation of Snyder and Smith (*ibid.*, 1944, **66**, 350). Moreover, the compound (II) is insoluble in dilute hydrochloric acid and does not give any test for free amino group. The compound (III), when subjected to the Dakin and West reaction with acetic anhydride in presence of pyridine, has readily furnished the corresponding ketone (V). However, by treating (V) with phosphorus oxychloride in nitrobenzene at 170°-180°, a strong base has been isolated which is devoid of any ketonic property and remains unaffected when heated with palladium charcoal in tetralin at 240° for 3 hours.

The compound (V), which is a keto-amide of the type : R_1-CO-CH(R_2)-NH-CO-R_3, is capable of yielding on dehydration an oxazole derivative (cf. Robinson and co-workers, *J. Chem. Soc.*, 1909, **95**, 2167 ; 1912, **101**, 1297 ; 1913, **103**, 1768). That the compound obtained by treatment of (V) with phosphorus oxychloride is not an oxazole derivative, but probably an *iso*quinoline derivative, is borne out by its strong basic character (cf. Robinson *et al.*, *loc. cit.* Young and Robinson, *J. Chem. Soc.*, 1933, 275) and also by analytical data. Further, it has been observed that (V), when treated with concentrated sulphuric acid under the usual mild conditions (namely, warming on the water-bath for 2 minutes) as generally employed by Robinson and his co-workers (*loc. cit.*), remains unchanged and is recovered on dilution with water. It is, however, significant to have observed that when a solution of (V) in concentrated sulphuric acid, after being allowed to stand at room temperature for 1½ hours, is heated at 98°-100° for about 10 minutes and then diluted with cold water, no precipitate of the expected oxazole derivative is obtained. On basification a solid has been obtained, which is found to be identical with the strong base obtained by treatment of (V) with phosphorus oxychloride, as described above.

During the Bischler-Napieralski cyclisation of acylamines, a part of the acylamine is sometimes hydrolysed to the amine (Decker *et al.*, *Annalen*, 1913, **395**, 299). If the compound (V) has suffered such hydrolysis, the amino-ketone, so formed, might yield a pyrazine derivative by aerial oxidation of the corresponding dihydropyrazine, first formed (cf. Gabriel, *Ber.*, 1908, **41**, 1127 ; Tutin, *J. Chem. Soc.*, 1910, **97**, 2500). Pyrazine derivatives, however, are found to be weakly basic, the hydrochlorides being readily dissociated in water (cf. Tutin, *loc. cit.*). Even the picrate of 2 : 5-dimethyl-3 : 6-diphenylpyrazine (Craig and Henze, *J. Org. Chem.*, 1945, **10**, 10) is unstable and reverts to the pyrazine when washed with water. These observations preclude the

formulation of the strong base, obtained from (V) by the action of phosphorus oxychloride or concentrated sulphuric acid, as a pyrazine derivative.

However, the behaviour of the compound (V) towards phosphorus oxychloride, resulting in the isolation of a strong base devoid of ketonic property and probably dehydrogenated, strikingly resembles that of N-acetylphenylalanine, which, when treated with a mixture of phosphorus oxychloride and polyphosphoric acid, yields 1-methyl*iso*quinoline as the only isolable product (Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2962). These findings, coupled with analytical data, strongly suggest that the strong base in the present case is 7-nitro-1-methyl*iso*quinoline (VI), formed, in an analogous manner, by the process of cyclisation, dehydrogenation and deacetylation. The exact sequence of the three processes involved is not, however, clear (cf. Snyder and Werber, *loc. cit.*). In an approach (cf. Galat, *ibid.*, 1953, **75**, 1738) to synthesise by an unambiguous method the formulation (VI), the Bischler-Napieralski cyclisation of (I) has now been attempted under varying conditions with phosphorus oxychloride or phosphorus pentoxide, but without success. (IV) also could not be induced to undergo the Bischler-Napieralski cyclisation under the influence of phosphorus oxychloride or phosphorus pentoxide. However, it has now been observed in an analogous case that (α-acetamido-β-phenyl)-ethylmethyl ketone (Cleland and Niemann, *ibid.*, 1949, **71**, 841) on the Bischler-Napieralski cyclisation under conditions as employed in the case of (V), yields a base identified to be 1-methyl*iso*quinoline through its picrate. This finding leaves no doubt about the formulation (VI) for the base obtained from the *p*-nitro analogue (V) under similar conditions.



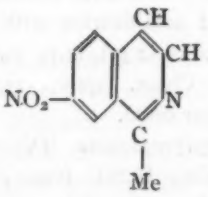
I, R_1, R_2 = —CO_2Et

II, R_1, R_2 = —CO_2H

III, R_1 = H, R_2 = —CO_2H

IV, R_1 = H, R_2 = —CO_2Me

V, R_1 = H, R_2 = —COMe



(VI)

From the results emerging out of the above experiments it would seem rather unpromising to attempt the preparation of a 3-acetyl-3 : 4-dihydro*iso*quinoline along the present route. It is also significant to note that the keto-amide (V), which is capable of yielding an oxazole derivative, furnishes, however, under the conditions as specified above, an *iso*quinoline derivative.

EXPERIMENTAL

Ethyl acetamidomalonate was prepared from *iso*nitrosomalonic ester (Snyder and Smith, (*loc. cit.*) with modification. A mixture of *iso*nitrosomalonic ester (260 g.), glacial acetic acid (1070 c.c.), acetic anhydride (350 c.c.) and CCl_4 (45 g.) was gradually treated under brisk stirring with zinc dust (360 g.) during 3 to 4 hours, the temperature being maintained at 40°-45° by external cooling. After addition of zinc dust was over the stirring was continued for one hour more, and the mixture filtered. After washing the residue with glacial acetic acid (200 c.c.) the filtrate and the washing were combined, diluted with cold water (1 litre) and extracted with chloroform. After removal of chloroform and acetic acid by distillation in an oil-bath under mild suction, the residue was cooled in ice, when a crystalline solid was obtained. This was filtered under suction, pressed and crystallised from water (charcoal) in colorless plates (188 g.), m.p. 97°. From the filtrate some more quantity (16 g.) of the substance was recovered.

Ethyl α-Carbethoxy-α-acetamido-β-p-*nitrophenylpropionate* (I).—Sodium (0.7 g.) was dissolved in anhydrous ethanol (16 c.c.) and to the cooled solution ethyl acetamidomalonate (6.8 g.) was added all at a time. To this mixture *p*-nitrobenzyl chloride (5.5 g.) was added under shaking, when heat was evolved and a solid separated. After refluxing on the water-bath for 10 hours, the mixture was diluted with water and the solid filtered, washed and crystallised from ethanol in cream-coloured needles (7 g.), m.p. 179-80°. (Found : N, 7.68. $C_{16}H_{20}O_7N_2$ requires N, 7.95 per cent).

α-Carboxy-α-acetamido-β-p-*nitrophenylpropionic Acid* (II).—The above compound (I, 7.5 g.) was treated with a solution of caustic soda (2.6 g.) in water (26 c.c.) and the mixture refluxed on the water-bath for about 5 hours. The deep red solution was just acidified, under cooling, with HCl (conc.) and the precipitated solid crystallised from aqueous ethanol in reddish brown micro-crystalline powder (3 g.), m.p. 148-50° (decomp.). (Found : N, 9.12. $C_{12}H_{12}O_7N_2$ requires N, 9.46 per cent).

α-Acetamido-β-p-*nitrophenylpropionic Acid* (III).—A mixture of the compound (II, 4 g.) and water (45 c.c.) was heated under reflux on the wiregauze for about 4 hours and the solution cooled in ice. The brown solid obtained was purified by solution in cold sodium bicarbonate solution and acidification with HCl (dilute). The solid was crystallised from water in yellowish needles (2 g.), m.p. 196-98°. It was dried at 100°-105° *in vacuo* over P_2O_5. (Found : Chem. equiv., 251.4 ; N, 11.34. $C_{11}H_{12}O_5N_2$ requires chem. equiv., 252 ; N, 11·11 per cent).

Methyl α-Acetamido-β-p-*nitrophenylpropionate* (IV).—A solution of (III, 13 g.) in anhydrous methanol (70 c.c.) containing H_2SO_4 (conc., 0.7 c.c.) was refluxed on the water-bath for 6 hours. After distilling most of the methanol, the residue was poured into water. The solid was triturated with 5% aqueous sodium bicarbonate solution, washed with water and crystallised from methanol in brownish needles (9.5 g.), m.p. 86-88°. (Found : N, 10.36. $C_{12}H_{14}O_5N_2$ requires N, 10.52 per cent).

(*α-Acetamido-β*-p-*nitrophenyl*)-*ethylmethyl Ketone* (V).—A mixture of (III, 10 g.), acetic anhydride (16 g.) and pyridine (16 g.) was heated under reflux on the water-bath for about 5 hours. Pyridine and excess of acetic anhydride were removed by steam

distillation and the mixture cooled in ice. The separated solid was filtered, washed with 10% aqueous sodium bicarbonate solution and crystallised from ethanol in brownish needles (5.6 g.), m.p. 149-50°. (Found : C, 58.18 ; H, 5.42 ; N, 11.46. $C_{12}H_{14}O_4N_2$ requires C, 57.6; H, 5.6 ; N, 11.2 per cent).

2 : 4-*Dinitrophenylhydrazone* crystallised from ethanol in brown needles, m.p. 268-70°. (Found : N, 19.14. $C_{18}H_{18}O_7N_6$ requires N, 19.53 per cent).

Action of Phosphorus Oxychloride on (V) : *Formation of* 1-*Methyl*-7-*nitroisoquinoline* (VI).—A mixture of (V, 12 g.), nitrobenzene (40 g.) and phosphorus oxychloride (20 c.c.) was gradually heated under reflux in an oil-bath and the temperature of the bath was maintained at 170°-180° for about 12 hours. The mixture was cooled and treated, under shaking, with ice and water. After separating the aqueous layer, the nitrobenzene layer was filtered from suspended impurity and extracted with cold HCl (5%). The aqueous layer and the acid extract were combined, treated with charcoal, filtered and just basified with caustic soda solution. The precipitated solid was crystallised from aqueous ethanol or petroleum ether (b.p. 60°-80°) in fine, colorless, slender needles (6.5 g.), m.p. 117-18°. It was dried at 90°-95° *in vacuo* over P_2O_5. (Found : C, 63.47; H, 4.68 ; N, 14.78. $C_{10}H_8O_2N_2$ requires C, 63.83 ; H, 4.25 ; N, 14.89 per cent). It is readily soluble in cold dilute hydrochloric acid and other mineral acids and does not give any test of ketonic group. It remained unaffected when heated with palladium-charcoal (5% Pd) in tetralin at 240° for 3 hours.

The *picrate* was obtained from benzene solution as yellowish brown needles, m.p. 159-60°. (Found : N, 16.43. $C_{10}H_8O_2N_2$, $C_6H_3O_7N_3$ requires N, 16.78 per cent).

Action of Concentrated Sulphuric Acid on (V) : *Formation of* (VI).—A solution of (V, 1 g.) in H_2SO_4 (5 c.c., *d* 1.48) was allowed to stand at room temperature for 1½ hours, heated on a water-bath at 98°-100° for about 10 minutes, cooled and then poured into cold water. The clear solution on basification with alkali solution yielded a solid (0.3 g.), which after crystallisation from aqueous ethanol was proved to be identical with (VI) by m.p. and mixed m.p. The identity was also confirmed by the m.p. of the picrate and a mixed m.p.

Action of Phosphorus Oxychloride on (α-*Acetamido*-β-*phenyl*)-*ethylmethyl Ketone* : *Formation of* 1-*Methylisoquinoline*.—A mixture of (α-acetamido-β-phenyl)-ethylmethyl ketone (12 g., Cleland and Niemann, *loc. cit.*), nitrobenzene (50 c.c.) and phosphorus oxychloride (30 c.c.) was heated in an oil-bath at 140°-150° for 2 hours and then at at 170°-180° for 20 hours. After cooling, the mixture was treated with ice-water, basified with concentrated caustic soda solution and then acidified with concentrated hydrochloric acid. The mixture was filtered from little tarry matter and the filtrate shaken twice with ether to remove nitrobenzene. The clear aqueous solution was basified with caustic soda solution under cooling and then extracted with ether. Removal of ether from the ethereal extract left a heavy liquid (3.5 g.) with characteristic basic odour, boiling at 248°-250° at ordinary pressure to give a colorless mobile liquid. It is readily soluble in cold dilute mineral acids and insoluble in water.

The *picrate* was obtained by warming a methanolic solution of the base with picric acid, cooling and scratching. It was crystallised thrice from methanol and obtained as yellow rectangular plates, m.p. 223-25°. (Found : N, 14.78. $C_{10}H_9N$, $C_6H_3O_7N_3$ requires N, 15.05 per cent), the m.p. being undepressed on admixture with an authentic sample.

The authors record their appreciation of the interest taken in this work by Dr. U. P. Basu, Director of the Institute.

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A NEW STAGE IN THE QUANTITATIVE REDUCTION OF PERMANGANATE IN ALKALINE SOLUTIONS (Mn_3O_4)

By I. M. Issa and S. A. Awad

Reduction of potassium permanganate with bivalent tin in weakly alkaline solutions leads to the formation of Mn_3O_4. It is found that the reaction proceeds so rapidly that it could be easily followed potentiometrically. When oxidation of bivalent tin is complete a sharp change in potential occurs. The reaction proceeds quantitatively with respect to the bivalent tin of concentrations ranging from 4.92×10^{-2} to 1.63×10^{-3} g. at./litre. Provided that the reactants are freed from dissolved oxygen and the titration performed in a stream of nitrogen, it could be used for potentiometric estimation of bivalent tin. When permanganate, not freed from oxygen, is used, its volume consumed is dependent on the rate of titration. This was not, however, the case if oxygen was excluded.

As is well known, reduction of potassium permanganate in alkaline solutions takes place in two well defined steps, viz., reduction to manganate at high alkali concentrations or to manganese dioxide at lower ones (Holluta, *Z. physikal. Chem.*, 1922, **101**, 34; **102**, 32, 276; **101**, 489; 1924, **113**, 464; Stamm, *Z. angew. Chem.*, 1934, **47**, 579; "Newer Methods of Volumetric Analysis" trans. by Oesper, von Nostrand Co. Inc., New York, 1938). In order to find out whether these reactions could be applicable generally to all reducing substances, we tried some of these, such as formate (*Anal. chim. Acta*, 1954, **10**, 192) tellurite (Issa and Awad, *Analyst*, 1953, **78**, 487) as well as plumbite (Issa, Issa and Abdel Azim, *Anal chim. Acta* 1954, **10**, 474) and found that in all cases the reduction proceeded in accordance with the above rule. With bivalent tin, on the other hand, a new product was formed which, as will be seen below, was proved to be Mn_3O_4. Reduction of MnO_4^- to Mn_3O_4, at low alkali concentration, with sodium stannite can be represented by the equation,

$$6MnO_4^- + 3H_2O + 13SnO_2^{2-} \longrightarrow 2Mn_3O_4 + 13SnO_3^{3-} + 6\ OH^- \quad \ldots\ (1)$$

That this reaction took place quantitatively was confirmed by calculating, by the aid of the following equations:

$$\log K = \frac{n(E_{01} - E_{02})}{0.059} \quad \text{and} \quad \alpha = K^{1/(Z_1+Z_2)},$$

the equilibrium constant, K, and the degree of completion, α, from a knowledge of the E_0 values of the systems under consideration. Z_1 and Z_2 are the valency changes of both ionic species and n, the number of Faradays necessary to complete the reaction; E_{01} and E_{02} are the redox potentials of the MnO_4^-/Mn_3O_4 and SnO_2^{2-}/SnO_3^{3-} systems. E_{02} amounts to -0.96 (Latimer "Oxidation Potentials", Prentice Hall, New York, 1938, p. 138) and E_{01} as calculated from free energy data (cited in Latimer, *op. cit.*, pp. 305, 331; Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances", Reinhold, New York, 1936, p. 93) for the reaction,

$$3\ MnO_4^- + 8\ H_2O + 13\ e = Mn_3O_4 + 16\ OH^- \quad \ldots\ (2)$$

amounts to -0.5535 volt.

K and α for reaction (1) amount accordingly to $10^{-178\cdot9}$ and $10^{-25\cdot26}$, indicating that the reaction can take place quantitatively to its end-point. In this investigation we are going to study the reduction of potassium permanganate with sodium stannite in view of working out the conditions favouring a quantitative reaction.

Experimental

The Titration Device.—Since bivalent tin is very sensitive, especially in alkaline media, to atmospheric oxygen, the titrations were performed in an atmosphere of pure nitrogen, freed from any oxygen contamination by a procedure similar to that of Hacourt and Lupton (*Chem. News*, 1876, **33**, 90). The titration vessel consisted of a well steamed pyrex glass beaker fitted with a rubber stopper that had been previously boiled in dilute hydrochloric acid. The stopper had holes for the tip of the burette, the stirrer with its mercury seal, the indicator electrode consisting of a platinum sheet 2 sq. cm. in area, the salt bridge filled with saturated potassium chloride solution and for the entrance and exit of pure nitrogen. As a standard half element, the saturated calomel electrode was used.

Preparation and Standardisation of Solutions: (*a*). *Potassium permanganate solutions.*—These were prepared by dissolving the appropriate weight of the purest grade in twice distilled water. The solutions were filtered through a sintered glass funnel of finest pore size to get rid of any manganese dioxide and then stored in dark-coloured bottles. They were standardised with sodium oxalate of grade "AnalaR" following the procedure recommended by Fowler and Bright (*J. Res. Nat. Bur. Standards*, 1935, **15**, 493). Solutions of lower concentrations ranging from 0.0774 N to 0.00774 N were prepared by accurate dilution so as to be comparable with those of the bivalent tin solutions to be titrated. From the change in valency of manganese, amounting to $4\frac{1}{3}$, the normality of potassium permanganate in this reaction is 13/15 of that corresponding to its reduction to the manganous state.

(*b*). *Bivalent tin solutions* were prepared by dissolving "Kahlbaum" stannous chloride in concentrated hydrochloric acid. The mixture was heated and kept in contact with a spectroscopically pure tin rod until it became absolutely clear. It was then delivered to a Zintl storage apparatus, a current of purified nitrogen was bubbled through for 30 minutes, and the solution then kept under pure nitrogen. Tin was estimated with potassium iodate of grade "AnalaR", using "AnalaR" chloroform as a solvent for the liberated iodine. The bivalent tin solutions, so prepared and stored, were found to be quite stable and suffered only very slight changes with time. This method of standardisation has been adopted as it possesses several advantages, viz., (*a*) potassium iodate solutions react quantitatively with stannous chloride, (*b*) the end-point is very sharp and (*c*) extreme precautions need not be taken to prevent atmospheric oxidation if the bulk of the iodate solution is added rapidly at first. Oxidation with dichromate of bivalent tin, on the other hand, is subject to some criticism in that the volume consumed changes with speed of the titration (Mülier and Stein, *Z. Elektrochem.*, 1930, **36**, 376). From the storage apparatus 10 ml. of the stannous chloride solutions were delivered into a conical flask containing a mixture of water and hydrochloric acid, freed from dissolved oxygen by bubbling nitrogen through. The bivalent tin solution

to be titrated with the iodate solution was 5*N* with respect to the acid. Under these conditions reduction of iodate yields ICl (Andrew, *Z. anorg. Chem.*, 1903, **36**, 76; *J. Amer. Chem. Soc.*, 1903, **25**, 756). The iodate solution was added rapidly at first with vigorous shaking and then slowly till the chloroform layer became colorless.

Solutions of lower concentrations (0.069 *N* to 0.0032 *N*) were prepared by diluting the accurately standardised solution with oxygen-free 5 *N* hydrochloric acid and then stored as usual in a Zintl storage apparatus under nitrogen.

Performance of the Titration with Potassium Permanganate.—Stannous chloride solution (10 ml.) was delivered from the Zintl storage apparatus into the titration vessel on to a volume of 18*N*-NaOH which was slightly less than that necessary for complete dissolution of the stannous hydroxide, and freed from dissolved oxygen by bubbling purified nitrogen through. To this was added an 18*N*-NaOH solution dropwise until the precipitated stannous hydroxide dissolved completely yielding sodium stannite (Hantzsch, *Z. anorg. Chem.*, 1902, **30**, 1902, 289) and the latter then titrated with potassium permanganate. The sodium hydroxide solution used was prepared by dissolving some of the solid metarial in an equal weight of water and leaving it until all the carbonate present had settled down.

TABLE I

	Amount of tin (g./litre). Present.	Found.	% Error.
(1) Slow addition 1 ml. at a time	5.8875	5.5670	−5.40
(2) „ „ 2 „ „	7.1814	7.0152	−2.52
(3) Rapid „ 5 „ „	5.8875	5.7213	−2.82
(4) 95% of $KMnO_4$ added one time	5.8875	5.8104	−1.30
(5) 98% „ „ „	5.8875	5.8875	±0

TABLE II

Amount of tin (g./litre). Present.	Found.	% Error.
5.8831	5.8104	−1.4
4.0952	4.0952	±0
0.3561	0.3552	−0.27
0.3561	0.3575	+0.4
0.4273	0.4268	−0.12
0.3082	0.3074	−0.38
0.1929	0.1917	−0.63

TABLE III

Amount of tin (g./litre). Present.	Found.	% Alkali in excess to stannite formation.	% Error.
4.0952	4.0952	0	±0
4.0952	4.0775	15	−0.43
4.0952	4.1325	25	−0.91
4.0952	4.2198	40	+3.00

DISCUSSION

When potassium permanganate was added to the stannite solution, a dirty yellow precipitate with a slight tinge of red was thrown down. The equilibria were rapidly attained and the potentials remained approximately constant till the end-point corresponding to the complete oxidation of stannite was reached, as evidenced by a sharp change in potential amounting to 400 millivolts per 0.1 ml. of the permanganate solution. It is noteworthy that before this end-point, the colour of the precipitate

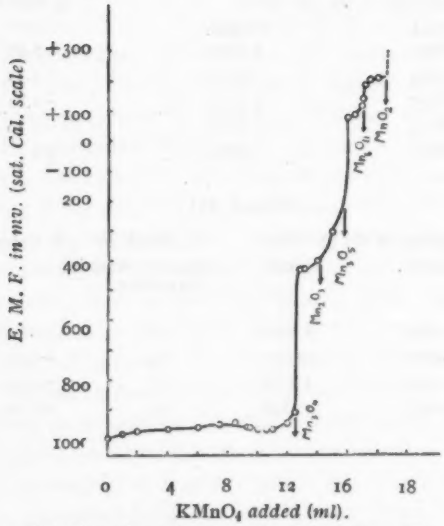
remains unchanged. By further addition of potassium permanganate thereafter, the colour of the precipitate becomes brown indicating that the primarily formed oxide undergoes oxidation to a higher one. Just after the end-point the equilibria are slowly attained and become rather slower at later stages, needing sometimes 10 minutes or more after each addition. This rendered continuing the potentiometric titration to the manganese dioxide stage, a tedious operation, apparently due to the fact that the reaction after the first jump involves the oxidation of a solid compound. The first stage in the reduction of $KMnO_4$ till the first inflection corresponds to the formation of Mn_3O_4 as evidenced by the following facts:

(1) The colour of the precipitate formed corresponds to that of manganosic oxide, Mn_3O_4.

(2) Calculation of the bivalent tin concentration on this basis leads to results coinciding with those obtained by the iodate method.

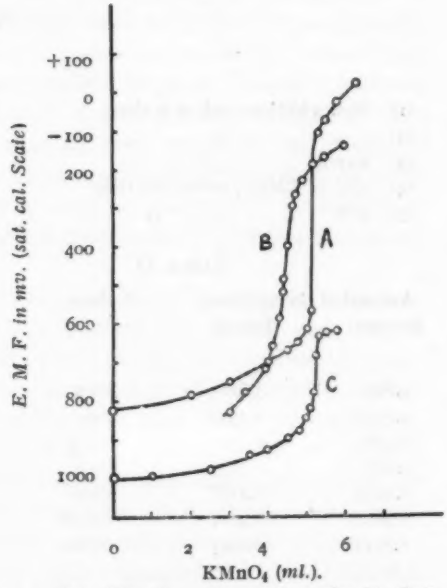
(3) After the inflection point corresponding to Mn_3O_4, breaks in the titration curve reveal themselves, corresponding to one or more of the higher oxides of manganese, e.g. Mn_2O_3, Mn_3O_5, Mn_6O_{11}, prior to the formation of MnO_2 (Fig. 1).

FIG. 1



Titration of 10 ml. of 0.122*N* Sn'' soln. with 0.0882*N*-$KMnO_4$ not freed from dissolved oxygen (error = 5.4%).

FIG. 2



(A) Titration of 10 ml. 0.0690 *N* Sn'' solution with 0.13416 *N*-$KMnO_4$ solution, alkali just sufficient to yield sodium stannite.

(B) Titration of 10 ml. 0.0060 *N* Sn'' solution with 0.013416 *N*-$KMNO_4$ solution, alkali used similar to A.

(C) Titration of 10 ml. 0.0690 *N* Sn'' solution with 0.13416 *N*-$KMnO_4$ solution, alkali added in excess = 25%.

In Tables I and II are recorded the results obtained under various conditions. The amounts of alkali used in these experiments are just sufficient to bring about complete dissolution of the precipitated stannous hydroxide. In Table I the titrations are made with potassium permanganate, not freed from dissolved oxygen, whereas those in Table II are performed with this reagent after removing dissolved oxygen by bubbling through pure nitrogen.

In experiment No. 1 (Table I) the titrant was added 1 ml. at a time to the stannite solution while bubbling through purified nitrogen till the end-point was approached. In this case the end-point was reached 5.40% earlier due perhaps to the interference of oxygen, dissolved in the permanganate solution, that oxidised part of the tin persent.

Since the redox potentials of the permanganate systems are higher than those of the oxygen electrode both in acid and alkaline media, the former will react before oxygen. The error due to dissolved oxygen can accordingly be minimised by adding larger portions of permanganate. The effect of oxygen can be minimised by bubbling purified nitrogen in the stannite solution.

Experiment No. 2 was performed by adding 2 ml. at a time till the end-point was approached. In this case the error decreased to 2.5%. By increasing the rate of addition still more, e.g. by adding 5 ml. at a time, the error became also smaller than in experiment No. 1 (experiment No. 3).

Experiment No. 4 was made by adding, at one time, 95% of the whole amount necessary for the attainment of the end-point, and then completing the titration. Under these conditions the error was only 1.3%. By adding 98% of the theoretical volume at one time, theoretical and the experimental amounts of tin coincided together (experiment No. 5).

In order to test the validity of the above assumption concerning the effect of oxygen dissolved in potassium permanganate on the results, the latter solutions were freed from dissolved oxygen and stored in a Zintl storage apparatus. The results recorded in Table II representing titrations made under these conditions indicate that the errors are small, despite the fact that the titrant is added in small portions. The concentration of the tin solution titrated varied from 1.63×10^{-3} to 4.99×10^{-2} g. at./litre. Accordingly, these processes involving the oxidation of bivalent tin with alkaline permanganate can be applied for the determination of small amounts of tin with fair degree of accuracy.

Curves A, B and C in Fig. 2 represent titrations of different amounts of tin with potassium permanganate in the absence of atmospheric oxygen. These curves are characterised by sharp breaks amounting in the case of the more concentrated solutions to 350-400 millivolts per 0.1 ml. of titrant and decreasing with declining tin concentration. As already stated, the end-point corresponds to the reduction of potassium permanganate to manganosic oxide, Mn_3O_4. The amounts of tin calculated on the basis of its formation coincide fairly well with those determined by iodate. In the more concentrated solutions (curve A) the potentials set change at first slowly with the permanganate addition till the end-point is reached. With more dilutions, on the other hand, (curve B), the potentials change more rapidly.

Effect of Alkali on the Results.—In Table III are shown the results obtained on adding varying amounts of alkali in excess to that necessary for the formation of sodium stannite. As may be seen from these results, small errors are observed when the alkali added in excess amounts to 15%. By increasing the alkali still further, the errors increase appreciably, the inflections at the end-points decrease (curve C, Fig. 2) and the colour of the precipitate becomes brownish due to the formation of some Mn_2O_3. At higher alkalinities the curves are quite irregular.

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AN EXPLANATION OF THE VARIATION OF ELECTROPHORETIC VELOCITY OF OIL DROPLETS OBSERVED BY MOONEY ON THE BASIS OF SURFACE CONDUCTIVITY CORRECTION

By B. N. Ghosh, K. C. Ray and P. B. Roychowdhury

It has been shown that the increase of the electrophoretic velocity of fine oil droplets with the increase of their radius, observed by Mooney, can be quantitatively accounted for on the basis of surface conductivity correction.

It has been reported by Mooney (*Phys. Rev.*, 1924, **23**, 396 ; *J. Phys. Chem.*, 1931, **35**, 331) that the electrophoretic velocity of fine droplets increases with their size. This has been attributed by him to the increase in the ratio of the radius, a, to the thickness, $1/k$, of the electrical double layer of the droplets. It follows from the analysis of Henry (*Proc. Roy. Soc.*, 1931, **A133**, 106) that for a solid insulating particle, when $ka > 100$, any further increase of ka would affect the electrophoretic velocity only slightly. An examination of Mooney's data, however, indicates that the electrophoretic velocity of the droplets increases markedly with a, even when $ka > 100$. Other alternative explanation of his observation therefore deserves careful consideration. According to Henry (*Trans. Faraday Soc.*, 1948, **44**, 1021) and Booth (*ibid.*, 1948, **44**, 455), when ka is sufficiently large, the electrophoretic velocity, U, of an insulating particle depends on its radius, a, and specific surface conductivity, χ, and is given by the following expression

$$U = \frac{DE\zeta}{4\pi\eta}\left\{\frac{S}{S+\chi/a}\right\} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where E is the potential gradient, ζ, the true electrokinetic potential, η is the viscosity of the liquid and S, its specific conductivity in bulk.

Putting ζ_a for $4\pi\eta U/DE$ and rearranging, equation (1) can be written as

$$\frac{1}{\zeta_a} = \frac{1}{\zeta}\left(1 + \frac{\chi}{Sa}\right) \quad \ldots \quad \ldots \quad (2)$$

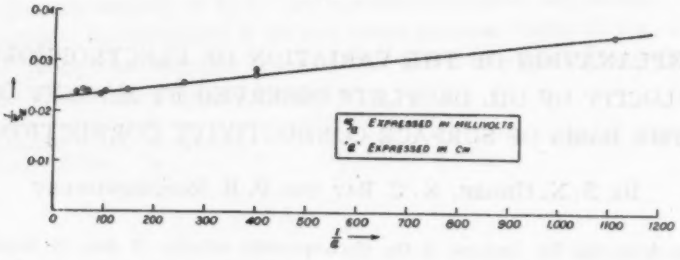
$$= 1/\zeta + m/a \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where $m = \chi/\zeta S$.

It is evident from equation (3) that the plot of $1/\zeta_a$ against $1/a$ should give a straight line, when $\chi/\zeta S$ is constant. Equation (3) has been applied to the electrophoresis of the fine oil droplets investigated by Mooney on the assumption that they behave as solid insulating particles possessing appreciable surface conductivity.

Explanation of the Figure and the Tables.—In Fig. 1 the values of $1/\zeta_a$ and $1/a$ of the droplets of Red oil and benzyl chloride have been plotted; the data necessary

FIG. 1



for this purpose were obtained from Fig. 1 of Mooney (*loc. cit.*, 1931). In Tables I, II and III are recorded the electrophoretic data found from the curves I, II and III of Fig. 5 of Mooney (*loc. cit.*, 1924) for stanolind (a paraffin hydrocarbon like Nujol). The values of electrophoretic velocity of the droplets of different radius found in distilled water containing electrolytic impurities of the order of $2 \times 10^{-5}N$ are recorded in Table I, while those recorded in Tables II and III have been found by using $1 \times 10^{-4}N$ and $1 \times 10^{-3}N$ – NaOH respectively.

TABLE I

$\zeta = 90.91$ mv. $m = 1.08 \times 10^{-6}$.

Radius (a) $\times 10^3$.	$1/a \times 10^{-3}$.	U (mobility observed in micron).	ζ_a (obs.).	ζ_a (calc.).
0.055 cm.	18.18	2.29	32.6 mv	32.8 mv
0.087	11.44	2.95	41.9	42.8
0.289	3.46	4.15	58.9	67.8
0.601	1.67	5.24	74.4	78 1
0.710	1.41	5.13	72 9	79.9
1.092	0.91	6 01	85.2	83.6
1.502	0.67	6.12	86.8	85.4
1.775	0.56	6.66	94.6	86.2
2.020	0.50	6.55	93.0	86.6

TABLE II

$\zeta = 111.7$ mv. $m = 1.03 \times 10^{-6}$.

Radius (a) $\times 10^3$.	$1/a \times 10^{-3}$.	U (mobility observed in micron).	ζ_a (obs.).	ζ_a (calc.).
0.164 cm	6.11	4.91	69.8 mv	65.6 mv
0.273	3.66	5.57	79.1	78.7
0.546	1.83	6.22	88.4	92.6
1.119	0.89	7.10	100.8	101.3
1.174	0.85	6.99	99 2	101.7
1.474	0 68	7.21	102.3	103.6
1.720	0.58	7.32	103.9	104.8
1.829	0.55	7.64	108.5	105.2
2.157	0.46	7.10	100.8	106.2
2.211	0.45	7.54	107.0	106.2

TABLE III

$\zeta = 163.3$ mv. $m = 2.39 \times 10^{-7}$.

Radius (a) $\times 10^3$.	$1/a \times 10^{-3}$.	U (mobility observed in micron).	ζ_a (obs.).	ζ_a (calc.).
0.055 cm.	18.18	7.43	105.4 mv	95.6 mv
0.109	9.17	8.41	119.4	120.2
0.273	3.66	9.28	131.8	142.9
0.546	1.83	10.37	147.2	152.4
0.851	1.18	11.14	158.1	156.2
0.960	1.04	10.92	155.1	156.9
1.392	0.72	11.03	156.6	158.8

It will be evident from Fig. 1 that for the mixture of Red oil and benzyl chloride plot of $1/\zeta_a$ against $1/a$ gives a straight line in satisfactory agreement with equation (3). Assuming that the distilled water used by Mooney in this case was of the same quality as reported by him in his first paper (*loc. cit.*, 1924), it follows that $ka > 90$ even for the smallest droplets investigated. An examination of the data in Tables I, II and III also shows that the values of ζ_a observed agree fairly with those calculated from equation (3). Furthermore, assuming that the electrolytic impurity ($2 \times 10^{-5} N$) present in the distilled water is KCl, its specific conductivity is found to be about 3.42×10^{-6} mhos. Using these data, the specific surface conductivity of the droplets of stanolind of radius 8.74×10^{-5} cm. has been calculated from equation (2). It is found to be 3.4×10^{-10} mhos which so far as magnitude is concerned, appears to be of the right order.

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COMPLEX COMPOUNDS OF NICKEL AND COPPER WITH *p*-PHENETYLBIGUANIDE

By S. P. Ghosh and A. K. Banerjee

Complex compounds of nickel and copper have been prepared and their properties studied. Besides nickel- and copper-*p*-phenetylbiguanidinium hydroxides, a number of salts, namely chloride, bromide, iodide, sulphate and nitrate have been reported. The nickel complex base, the chloride and the sulphate have been obtained in two different modifications. This is attributed to the favourable "size factor" of the co-ordinating molecule. The copper complexes did not exhibit any such modifications. No reason could as yet be put forward for this behaviour.

Ghosh and Chatterjee (this *Journal*, 1953, **30**, 369) have described the complex compounds of copper and nickel with phenylmethylbiguanide. No evidence could be obtained for the *cis-trans* isomerism for the planar four-covalent complexes with this co-ordinating molecule, though the so-called 'size factor' appeared to be more favourable than phenylbiguanide in the case of which definite evidences for such isomerism were obtained by Rây and Chakravarty (*ibid.*, 1941, **18**, 609). In the present communication the nature of the complexes formed by nickel and copper with *p*-phenetylbiguanide is being reported. Rây and Chakravarty (*loc. cit.*) obtained a number of copper phenylbiguanide complexes in two different modifications, viz., chloride, bromide, iodide and sulphate. In the case of *para*-phenetylbiguanide complexes of copper, however, only one form of complexes could be prepared. Nickel *para*-phenetylbiguanide complexes, however, could be prepared in two different modifications in case of the base, the chloride and the sulphate. Rây and Chakravarty, in the case of the phenylbiguanide complexes, obtained the base only in two different modifications. It can thus be seen that though the phenylbiguanide molecule has been further weighted, it has little influence on the nature of the copper complexes, though in case of the nickel complexes we find a slight magnification of the effect. At this stage it is not possible to find out the effect of weighting the biguanide molecule on the nature of the complexes obtained till further work is done on substituted aromatic biguanides.

Experimental

p-Phenetylbiguanide hydrochloride ($C_{10}N_5H_{15}O.HCl$) was prepared according to the method of Cohn (*J. prakt. Chem.*, 1911, **84**, 400) by refluxing an equimolecular mixture of *p*-phenetidine hydrochloride and dicyandiamide in water for 2½ hours. The solution on cooling deposited white crystals of the hydrochloride which were purified by recrystallisation from hot water after treatment with bone charcoal, m.p. 208°.

Nickel Compounds

Nickel-phenetylbiguanidinium Hydroxide.—To a solution of nickel sulphate and *p*-phen ylbiguanide hydrochloride (2 mol.) a slight excess of ammonium hydroxide was

added dropwise. A slightly reddish buff coloured precipitate separated at once. This was rapidly filtered and washed with ice-cold water and alcohol and then dried over caustic soda to a constant weight. {Found : Ni, 10.27; N, 24.83. [Ni (*p*-phenetyl-BigH$^+$)$_2$]-(OH)$_2$ requires Ni, 10.27 ; N, 24.51 per cent} (where *p*-phenetyl-BigH = one molecule of *p*-phenetylbiguanide = $C_{10}N_5H_{13}O$). The dried sample was orange in colour and insoluble in water and alcohol. It liberates ammonia from ammonium salts and on a water-bath it changes to a sticky mass.

α-*Nickel*-p-*phenetylbiguanidinium chloride* was obtained as a light yellow precipitate when the complex base was tritrurated with ammonium chloride in the cold. When the evolution of ammonia had ceased, the crystals were filtered and washed with cold water and dried in the air. The substance is moderately soluble in hot water. {Found : Ni, 9.47 ; Cl, 11.40. [Ni (*p*-phenetyl-BigH$^+$)$_2$]Cl$_2$. 3H$_2$O requires Ni, 9.36 ; Cl, 11.35 per cent}. At 100° the loss in weight of the substance was 8.38%, the theoretical value for 3H$_2$O being 8.69%.

β-*Nickel*-p-*phenetylbiguanidinium Chloride*.—When the complex base was carefully neutralised with cold dilute hydrochloric acid, a dirty red precipitate was formed. This was filtered and washed thoroughly with cold water and dried in air. The dried sample was brick-red in colour. It is insoluble in water but on keeping in contact with water it slowly changes its colour to that of γ-variety, *i.e.* light yellow. {Found : Ni, 9.48 ; Cl, 11.23. [Ni (*p*-phenetyl-BigH$^+$)$_2$] Cl$_2$. 3H$_2$O requires Ni, 9.36 ; Cl, 11.35 per cent}.

Nickel-p-*phenetylbiguanidinium Bromide*.—Like the chloride, when the complex base was treated with a concentrated solution of ammonium bromide, a dirty brick-red precipitate was obtained which was filtered, washed with cold water and dried in air. It can also be prepared by the action of a concentrated solution of potassium bromide on the chloride. {Found : Ni, 8.14 ; Br, 22.46 ; H$_2$O (at 100°), 7.44. [Ni (*p*-phenetyl-BigH$^+$)$_2$]-Br$_2$.3H$_2$O requires Ni, 8.20 ; Br, 22.40 ; H$_2$O, 7.60 per cent}.

Nickel-p-*phenetylbiguanidinium iodide* was obtained as a light yellow mass when the complex base was treated with ammonium iodide. When the evolution of ammonia had ceased it was filtered, washed with cold water and dried in air. It is moderately soluble in alcohol. {Found : Ni, 7.10 ; I, 31.84 ; H$_2$O (at 100°), 6.53. [Ni(*p*-phenetyl BigH$^+$)$_2$] I$_2$.3H$_2$O requires Ni, 7.19 ; I, 31.84 ; H$_2$O, 6.67 per cent}.

α-*Nickel*-p-*phenetylbiguanidinium sulphate* was prepared by the action of ammonium sulphate on the complex base. A reddish cream-coloured mass slowly separated which was filtered, washed with cold water and alcohol and dried in air. The same can also be obtained by the action of potassium sulphate on the complex chloride. {Found : Ni, 8.82 ; SO$_4$, 14.70; H$_2$O (at 100°), 8.29. [Ni (*p*-phenetyl-BigH$^+$)$_2$] SO$_4$. 3H$_2$O requires Ni, 9.00 ; SO$_4$, 14.76 ; H$_2$O, 8.30 per cent}.

β-*Nickel*-p-*phenetylbiguanidinium sulphate* was obtained like the chloride as a dirty red mass when the complex base was carefully neutralised with dilute sulphuric acid. The substance was filtered, washed with cold water and alcohol and dried in air. The dried sample was brick-red in colour. {Found: Ni, 9.28 ; SO$_4$, 15.07 ; H$_2$O (at 100°), 5.30. [Ni (*p*-phenetyl-BigH$^+$)$_2$]SO$_4$. 2H$_2$O requires Ni, 9.26 ; SO$_4$, 15.18 ; H$_2$O, 5.68 per cent}.

Nickel-p-*phenetylbiguanidinium nitrate* was obtained as an orange-yellow substance when the moist base was treated with ammonium nitrate in the cold. It was filtered, washed with cold water and alcohol and dried in air. In an attempt to prepare it by the neutralisation of the base with dilute nitric acid, it was observed that the base decomposed. {Found : Ni, 8.82 ; N, 25.17 ; H_2O (at 100°), 5.39. [Ni (*p*-phenetyl-BigH$^+$)$_2$]-$(NO_3)_2.2H_2O$ requires Ni, 8.87; N, 25.42 ; H_2O, 5.44 per cent}.

Copper Compounds

Copper-p-*phenetylbiguanidinium hydroxide* was precipitated when an ammoniacal copper sulphate solution was added slowly to that of the *p*-phenetylbiguanide hydrochloride. The light violet precipitate was filtered and washed with water. It was purified by dissolving it in dilute HCl and reprecipitating with dilute ammonia. The precipitate was filtered, washed with cold water and alcohol and dried over caustic soda to a constant weight. {Found : Cu, 10.67 ; N, 23.25. [Cu (*p*-phenetyl-BigH$^+$)$_2$] $(OH)_2$. $3H_2O$ requires Cu, 10.70 ; N, 23.58 per cent}. The base is moderately soluble in alcohol. It liberates ammonia from ammonium salts.

Copper-p-*phenetylbiguanidinium Chloride*.—The moist complex base was treated with ammonium chloride on the water-bath. A pink coloured solution was obtained when the evolution of ammonia had ceased. The solution on cooling deposited pink crystals. These were filtered, washed with ice-cold water and dried in air. It is soluble in hot water. {Found : Cu, 9.67 ; Cl, 10.81 ; H_2O (at 100°), 12.30. [Cu (*p*-phenetyl-BigH$^+$)$_2$]-$Cl_2.4.5H_2O$ requires Cu, 9.66 ; Cl, 10.80 ; H_2O, 12.32 per cent}.

The complex *bromide* was obtained in the same way as the complex chloride by the treatment of the complex base with ammonium bromide. The substance was crystalline and deep pink in colour. It was washed as usual. {Found: Cu, 9.02 ; Br, 22.36; H_2O (by loss at 80°), 5.18. [Cu (*p*-phenetyl-BigH$^+$)$_2$]Br_2. $2H_2O$ requires Cu, 9.05 ; Br, 22.81 ; H_2O, 5.16 per cent}.

The complex *iodide* was obtained when the complex base was treated with ammonium iodide on the water-bath, as a flesh coloured mass. The substance was filtered and washed with cold water and dried in air. {Found: Cu, 8.33 ; I, 33.50. [Cu (*p*-phenetyl-BigH$^+$)$_2$] I_2 requires Cu, 8.37 ; I, 33.43 per cent}.

The complex *sulphate* was obtained by the action of ammonium sulphate on the complex base. It forms dark violet powder, sparingly soluble in water. It was also precipitated when the complex chloride was treated with potassium sulphate. It was washed and dried in the usual way. {Found: Cu, 9.33 ; SO_4, 14.26 ; H_2O, 10.46 by (loss at 110°). [Cu (*p*-phenetyl-BigH$^+$)$_2$ SO_4.] $4H_2O$ requires Cu, 9.38 ; SO_4, 14.30 ; H_2O, 10.76 per cent}.

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POTENTIOMETRIC TITRATIONS USING RESIN MEMBRANE ELECTRODES

By S. K. Sinha

Reversible resin membrane electrodes, prepared from ion-exchange resins, have been used in the potentiometric titrations of acid base, chloride and sulphate.

In previous communications (this *Journal*, 1954, **31**, 572, 577) by the author it has been shown that thin membranes prepared from ion-exchange resins can be used as reversible electrodes with respect to various cations and anions. In an earlier communication (*ibid.*, 1953, **30**, 529) some of the membrane electrodes were reported to be reversible with respect to H^+ ions, and the possibility of carrying out acid-base titrations with them had also been indicated.

Acid-Base Titrations

Since the measurement of hydrogen-ion activity was fairly satisfactory with IONAC-C-200 and RF-resins, they were chosen in this communication for the titration of an HCl solution with an NaOH solution. A solution of 0.1*N*-HCl (10 c.c.) was taken for this purpose and the same solution was placed on the inner side of the membrane. The solution was titrated with a normal alkali solution. The titration curves are shown in Fig. 1. The titre value agrees well with that obtained using an indicator.

The titration curves differ appreciably from the usual potentiometric ones in that they show absence of initial buffering as observed in the case of hydrogen or glass electrodes. Instead, the E.M.F. gradually rises. This appears to be due to difference in the 'mobility' of H^+ and Na^+ ions. Had the ratio u_{H^+}/u_{Na^+} (*loc.cit.*, p. 577) been equal to unity, there would not be any rise in the slope of the curve and the curve would have almost been parallel with the horizontal axis, *i.e.*, the usual buffering might have been observed. We may, however, eliminate the potential arising out of this difference in the mobility, if at each stage of the titration, this is subtracted from the observed potential. Let E_o be the observed potential and E_i, the initial potential, *i.e.*, the potential before titration. Now,

$$E_i = \frac{RT}{F} \ln \frac{a'_{H^+}}{a''_{H^+}}$$

and $E_o - E_i$ will be the potential difference between the observed potential and the initial potential at any stage of titration. The value of $E_o - E_i$ can, however, be calculated from theoretical considerations (Marshall, *J. Phys. Chem.*, 1944, **48**, 67).

$$E_o = \frac{RT}{F} \ln \frac{a''_{H^+}}{a'''_{H^+} + \frac{u_{Na^+}}{u_{H^+}} . a''_{Na^+}}$$

where a'''_{H^+} and a''_{Na^+} are the activities of hydrogen and sodium ions respectively at any stage of titration. Then $a'''_{H^+} + a''_{Na^+} = a''_{H^+}$, assuming the activity coefficients to be equal at high dilutions.

$$\therefore \Delta E_{theor.} = E_0 - E_i = \frac{RT}{F} \ln \frac{a^{I}_{H^+}}{a'^{II}_{H^+} + \frac{u_{Na^+}}{u_{H^+}} \cdot a^{II}_{Na^+}} \times \frac{a'^{II}_{H^+} + a^{II}_{Na^+}}{a^{I}_{H^+}}$$

$$= \frac{RT}{F} \ln \frac{a'^{II}_{H^+} + a^{II}_{Na^+}}{a'^{II}_{H^+} + \frac{u_{Na^+}}{u_{H^+}} \cdot a^{II}_{Na^+}}.$$

Hence $\Delta E_{theor.}$ can be calculated if we know the u_{Na^+}/u_{H^+} values for the membranes concerned. For IONAC C-200, the value for u_{H^+}/u_{Na^+} can be calculated from the values of

$$\frac{u_{K^+}}{u_{Na^+}} = 1.3 \text{ and } \frac{u_{H^+}}{u_{Na^+}} = 6.5$$

from Table V (*loc. cit.*, p. 572), so that

$$\frac{u_{H^+}}{u_{Na^+}} = \frac{u_{K^+}}{u_{Na^+}} \times \frac{u_{H^+}}{u_{K^+}} = 6.5 \times 1.3 = 8.45.$$

In 10.0 c.c. of a 0.1*N*-HCl solution to which 0.5 c.c. of an *N*-NaOH solution has been added

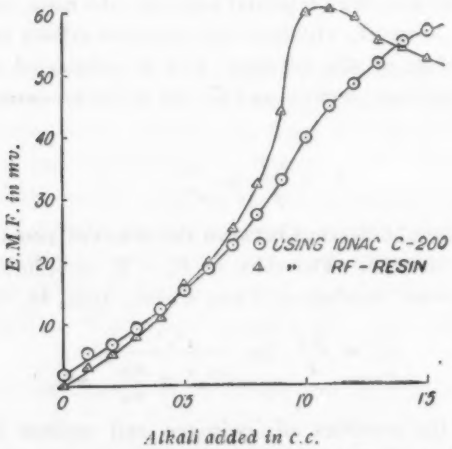
$$a'^{II}_{H^+} = 0.05$$
$$a^{II}_{Na^+} = 0.05$$

$$\therefore \Delta E_{theor} = 0.059 \log \frac{0.1}{0.05 + \frac{0.05}{8.45}} = 14.85 \text{ mv.}$$

$$\Delta E_{obs} = 13.5 \text{ mv.}$$

The agreement seems to be quite good and within about 1 mv. But such calculations are not necessary in the titration process since the inflexion in the curve is the most important consideration, and this is quite prominent in spite of the above complications.

FIG. 1.



If we could titrate an acid with a base containing a cation, which has the same 'mobility' as the hydrogen ion, we should get marked initial buffering as well as sharp

inflexion. The inflexion in the curve is due to the fact that up to the neutralisation point, the change in the potential is due to hydrogen ions being replaced by sodium ions, but at the neutralisation point, there is a sharp change in the hydrogen-ion concentration, and hence, the steep rise in the curve. At higher p_H the rate of change again becomes slow and the curve runs flat. As can be seen from Fig. 1, the curves with the RF-resin differ from the one with IONAC C-200 in that the E. M. F. 's decrease after the neutralisation point. This may be due to the RF-resin being not reversible with respect to hydrogen ions at higher p_H values, but to sodium ions.

The titration is perhaps possible in presence of small quantities of other ions, but large quantities of salts are likely to affect the inversion adversely.

Potentiometric Titrations with Membrane Electrodes from Anion-exchange Resins

Estimation of Chloride.—The reversibility of resin membrane electrodes, prepared from anion-exchange resins, with respect to chloride and sulphate ions has already been indicated (*loc. cit.*, 577). In the present paper such electrodes have been used for quantitative estimations of chloride and sulphate ions in solutions by potentiometric titrations against suitable standard solutions.

A high precision in the estimation of chloride ions by potentiometric titration was obtained by Lange and Schwartz (*Z. physikal. Chem.*, 1927, **129**, 111) and MacInnes and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1119). But great care and manipulative skill are necessary in setting up the Galvanic cells described by the above authors. On the other hand, the membrane electrodes, as we have seen (*loc.cit.*), are easy to set up, and the degree of accuracy observed with them will be clear from the results given below.

The titration curves of a sodium chloride solution with a standard silver nitrate solution, obtained by using IONAC A-300 membrane electrodes, saturated with respect to chloride ions, are shown in Fig. 2, where the observed E. M. F. 's are plotted against the volumes of silver nitrate added. The end-point in the titration is marked by a sharp inflexion in the curve and the titre value of the end-point is given by the point of intersection of the two curves. The estimated value of the chloride-ion concentration is found to be 1.0 m.e. where the actual amount taken is also 1.0 m.e. The titration is possible in presence of sulphate ions and the inflexion is as sharp as in the chloride solution alone, as will be evident from the curve in

FIG. 2.

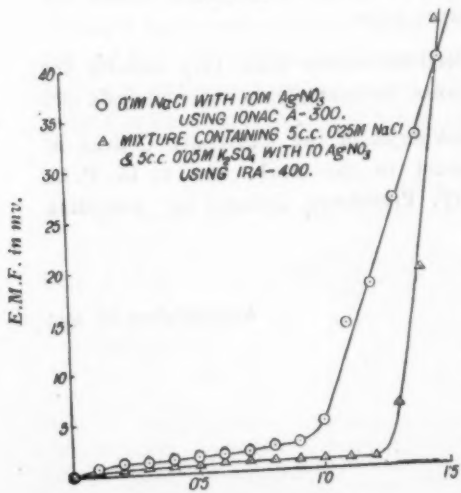
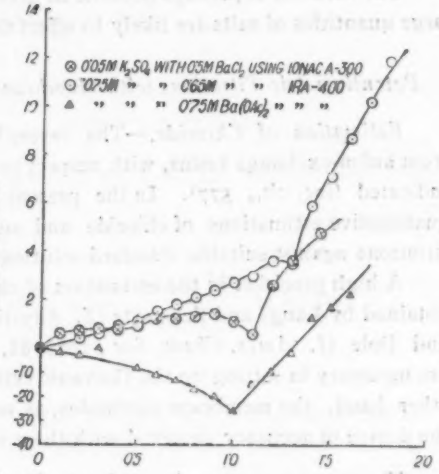


Fig. 2. The chloride content calculated from the curve is 1.26 m.e. whereas the actual value is 1.25 m.e.

Estimation of Sulphate.—Sulphate solutions have also been titrated against standard barium salt solutions using Amberlite IRA-400 electrodes saturated with sulphate ions. The titration curves are shown in Fig. 3. Using $BaCl_2$ solution as the titre, the inflexion occurs with a slightly higher amount of the titre than the theoretical. Moreover, it is not easy from the nature of the inflexion to get the exact end-point. The titration with Ba $(OAc)_2$ solution, however, gives a sharper end-point. Also, the curve obtained with $Ba(OAc)_2$ is quite different in nature (Fig. 3). Possibly, the membrane is not very sensitive to acetate ions, in presence of SO_4^{2-} ions, and hence, the E. M. F. at first diminishes as a result of decrease of sulphate ions, but near about the equivalence point the acetate ions begin to exert their influence, which suddenly becomes very large at the equivalence point. Further on, the rise in the E. M. F. is fairly steep.

FIG. 3.



The accuracy of determination of sulphate will be evident from Fig. 3, where the two curves meet almost at the theoretical equivalence point.

The ease of manipulation of the membrane electrodes makes them very suitable for use in solutions of low chloride and sulphate contents, for example, in water analysis etc.

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KINETICS OF CATION EXCHANGE REACTION IN SOLVENTS OTHER THAN WATER. PART I. EXCHANGE OF Cu^{2+} ION BY AMBERLITES IRC- 50 AND IR- 120

By R. P. Shukla and R. P. Bhatnagar

Kinetics of the exchange reactions of Cu^{2+} ion by Amberlite IRC-50 and IR-120 in non-aqueous solvents has been determined and the results show that the reaction fails to obey first and second order reaction mechanisms because H^+ ion formed start reversible reaction.

Kinetics of exchange reactions in water as solvent has been studied by many workers (Wiegner, *Trans. 3rd. Intern. Congr. Soil Sci.*, 1936, **3**, 5; Nachod and Wood, *J. Amer. Chem. Soc.*, 1944, **66**, 1380; Juda and Carron, Paper presented at the Division of Physical and Inorganic Chem., *Amer. Chem. Soc.*, Sep. 1947, etc.). Bodamer and Kunin (*Ind. Eng. Chem.*, 1953, **45**, 2577) studied the behaviour of ion exchange in solvents other than water, but their work was limited to ascertaining the swelling and exchange characteristics of the resins. Moreover, they did not use completely dried resin and the solvents were also mixed with a little water.

We have used resins (Amberlites IRC-50 and IR-120) in hydrogen cycle which were completely dried in a vacuum desiccator. They were then washed repeatedly with absolute alcohol to remove any adhering water and again dried in vacuum. Anhydrous, and pure cupric chloride was used as a solute.

Experimental

To study the kinetics, solutions (100 c.c.) of cupric chloride (anhydrous) in non-aqueous solvents were used and 2 g. of the particular resin added. The reaction was carried out in a thermostat (± 0.1°) and the reaction vessel was shaken continuously by magnetic stirrer. After a definite interval of time an aliquot was taken out and Cu^{2+} was estimated iodimetrically (titrating with thiosulphate after adding KI and 2 c.c. starch near the end-point). To get the sharp end-point a few c.c. distilled water was added to each aliquot before titration. The results are shown below.

Table I

Resin : Ambrelite -IRC-50.

(1). Temp. = 30.5°. Solvent : EtOH.

Time.	$a-x$.	x.	$\log\left\{\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right\}$	$K\times10^3$.
0.0 min.	8.15	...	...	...
24.0	8.10	0.05	0.0539	0.0136
105.0	7.95	0.20	0.2234	0.0132
165.0	7.85	0.30	0.3543	0.0134
210.0	7.80	0.35	0.4232	0.0144
Inf.	7.40	0.75 (x_e)	0.0	...

(2). Temp. = 40.1°. Solvent : EtOH.

Time.	$a-x$.	x.	$\log\left\{\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right\}$	$K\times10^3$.
0.0 min.	6.25	...	...	...
60.0	6.225	0.025	0.1060	0.0313
135.0	5.95	0.30	0.1976	0.0259
195.0	5.85	0.40	0.2719	0.0247
225.0	5.80	0.45	0.3117	0.0245
285.0	5.70	0.55	0.3972	0.0247
345.0	5.65	0.60	0.4441	0.0224
Inf.	5.1	1.15 (x_e)	...	...

Time.	$a-x$.	x.	$\log \left\{\frac{x(a-2x_0)+ax_0}{a(x_0-x)}\right\} K \times 10^2$		Time	$a-x$.	x.	$\log \left\{\frac{x(a-2x_0)+ax_0}{a(x_0-x)}\right\} K \times 10^2$	
(3). Temp. = 30.5°. Solvent : acetone.					(4). Temp. = 40.1°. Solvent : acetone.				
0.0	2.25	...	...	...	0.0	1.5	...	...	...
30.0	2.15	0.1	0.0506	0.299	15.0	1.475	0.025	0.0082	0.209
45.0	2.10	0.15	0.0778	0.310	45.0	1.45	0.05	0.0262	0.220
105.0	2.0	0.25	0.1368	0.292	105.0	1.40	0.10	0.0544	0.198
165.0	1.85	0.40	0.2407	0.250	165.0	1.35	0.15	0.0847	0.196
225.0	1.75	0.50	0.3245	0.256	225.0	1.30	0.20	0.1176	0.204
Inf.	1.25	1.0 (x_e)	...	...	285.0	1.25	0.25	0.1602	0.215
					Inf.	0.70	0.80 (x_e)	...	...

TABLE II

Resin = Amberlite IR – 120.

(I). Temp. = 30.6°. Solvent : EtOH.					(II). Temp. = 40°. Solvent : EtOH.				
0.0 min.	6.95	...	...	...	0.0 min.	5.20	...	...	...
15.0	5.85	1.1	0.0168	0.783	30.0	4.175	1.025	0.0085	0.136
45.0	4.50	2.45	0.0488	0.750	45.0	2.85	2.35	0.0287	0.153
60.0	3.75	3.20	0.0767	0.883	105.0	1.75	3.45	0.0686	0.157
105.0	3.15	3.80	0.1087	0.716	195.0	1.15	4.05	0.1232	0.151
165.0	2.45	4.50	0.2066	0.866	225.0	1.05	4.15	0.1385	0.151
225.0	2.05	4.90	0.2187	0.673	330.0	0.75	4.45	0.2120	0.154
Inf.	0.20	6.3 (x_e)	...	...	Inf.	0.20	5.00 (x_e)	...	...
(III) Temp. = 30.6°. Solvent : acetone.					(IV). Temp. = 40°. Solvent : acetone.				
0.0	2.20	...	...	...	0.0	2.85	...	...	...
30.0	2.05	0.15	0.0297	0.481	45.0	2.70	0.15	0.0619	0.188
45.0	2.00	0.20	0.0406	0.439	60.0	2.65	0.20	0.0898	0.194
105.0	1.80	0.40	0.0904	0.420	120.0	2.45	0.40	0.1842	0.215
165.0	1.70	0.50	0.12090	0.355	180.0	2.25	0.60	0.3089	0.235
285.0	1.45	0.75	0.2139	0.366	285.0	2.125	0.725	0.5141	0.245
Inf.	0.70	1.5 (x_e)	...	...	Inf.	1.60	1.25 (x_e)	...	...

N.B. (i) Readings for infinite time were taken after 3 days so as to ensure the establishment of complete equilibrium.
(ii) (a-x) is the volume in c.c. of thio required to titrate Cu^{2+} present in each aliquot at difinite time intervals.
(iii) Values of K are found out with respect to $\log_{10}$ values.

DISCUSSION

The reaction fails to obey ordinary first and second order reaction mechanisms because H^+ ions which are formed start the reversible reaction.

Let RH represent the resin in the hydrogen cycle; the reaction can then be written as

$$2\,RH + Cu^{2+} \rightleftarrows R_2Cu^2 + 2H^+ \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

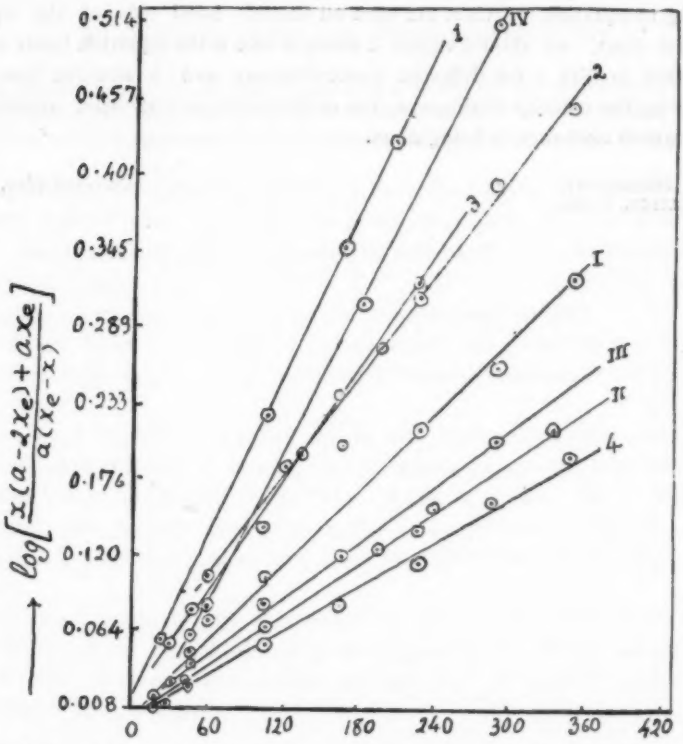
or

$$-\frac{dCu^{2+}}{dt} = K.RH \times Cu^+ - K'\,H^+R_2Cu \quad \ldots \quad \ldots \quad (2)$$

Initially only RH and copper ions are present at concentrations RH_0 and Cu^{2+}_0. Hence equation (2) becomes

$$-\frac{dCu^{2+}}{dt} = Cu^{2+}(RH^{+}_{0} - Cu_{0}^{2+} + Cu^{2+}) - K'(Cu_{0}^{2+} - Cu^{2+})^{2} \quad \ldots \quad (3)$$

FIG. 1



The number in the graphs corresponds to the readings of the same number in Tables I and II.

Integration can be done by using partial fractions, the final expression will be

$$\log \frac{(Cu_{0}^{2+} - Cu_{\infty}^{2+})\ (Cu^{2+} - Cu_{\infty}^{2+} + Q)}{(Cu^{2+} - Cu_{\infty}^{2+})\ (Cu_{0}^{2+} - Cu_{\infty}^{2+} + Q)} = (K - K')\,Qt \quad \ldots \quad \ldots \quad (4)$$

where Cu_{0}^{2+} = initial concentration of copper;
Cu^{2+} = change in concentration of copper at the time t;
Cu_{∞}^{2+} = change in concentration when equilibrium has reached or t = infinity;
while $Q = [1/(K-1)]\sqrt{K^{2}(RH_{0}^{+} - Cu_{\infty}^{2+})^{2} + 4Cu_{\infty}^{2+}RH_{0}K}$ and $K = k/K'$.

Putting x = change in concentration at time t, a = initial concentration (t=0), and x_{e} = change in concentration at t = infinity or when equilibrium has reached, equation (2) becomes

$$dx/dt = K'(a-x)^{2} - K'x^{2} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

and equation (4) becomes

$$\log\left[\frac{x(a-2x_{e}) + ax_{e}}{a(x_{e}-x)}\right] = K.\ \frac{2a\ (a-x_{e})}{x_{e}} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

Since the term $2a\ (a-x_e)/x_e$ is constant (k'), the equation (6) assumes the form

$$\log\left[\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right] = Kk't \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

According to equation (7) when the term on the left hand side of the equation is plotted against time, we should expect a straight line if the equation holds true. We have plotted this in Fig. 1 for different concentrations and a straight line has been obtained showing the validity of this equation of reversible second order reaction. Further work on anion exchange is being done.

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BASIC FLUOBERYLLATES. PART I. BASIC FLUOBERYLLATES OF COPPER, NICKEL AND ZINC

By Grihapati Mitra and Nirmalendunath Ray

The basic fluoberyllates of Cu, Zn and Ni have been prepared (1) by hydrolysis of a fluoberyllate solution at a comparatively low temperature and (2) by the action of metallic magnesium on fluoberyllate solution. One of the basic fluoberyllates is isomorphous with the corresponding basic sulphate.

Werner discussed the structure of basic salts in the light of his co-ordination theory and classified them in three types, viz., the hexol, the tetrol and the diol (*Ber.*, 1907, **40**, 4444). Basic salts are generally formed by cations of weak electropositive character or of small ionic volume, e.g., Cu^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+} etc. The nature of the anion also plays a very important part in the formation and stability of the basic salts. Beebe (*J. Phys. Chem.*, 1931, **35**, 3677) arranged the following ions in order of the stability of their basic salts: chloride > sulphate > trichloroacetate > nitrate, chlorate > acetate.

Again, though the basic chlorides are formed more easily, the number of basic bromides isolated in the case of copper, for instance, is greater than that of the basic chlorides (Feitknecht and Collet, *Helv. Chim. Acta*, 1939, **22**, 1428). The nature of the compound also depends upon the methods of preparation (Binder, *Ann. chim.*, 1936, **5**, 335), concentration of the solution (de Beco, *Bull. soc. chim.*, 1945, **12**, 795) and temperature.

Attempts were made in this laboratory to prepare the basic fluoberyllates and a number of them have been described in the present paper. These compounds persent particular interest in view of the fact that no basic salt of complex fluorides has yet been described in the literature.

Experimental

Methods of Preparation.—When the bright blue crystals of the pentahydrated copper fluoberyliate are left exposed to air for a few weaks, the colour becomes gradually dull and a light green insoluble layer is formed above the crystals. This insoluble layer contains basic fluoberyllate of copper but the amount is small and the product is far from pure. Of the various methods which were examined for the preparation of the basic fluoberyllates of the metals, the following led to successful results.

(*a*). A solution of the metallic fluoberyllate was heated on the water-bath with the addition of beryllium carbonate at intervals in small quantities. This helped to remove the acid resulting from hydrolysis. The volume of the solution was also kept constant by the addition of water to replenish the loss by evaporation. The temperature of the solution was also maintained at or below 60°, otherwise the basic fluoride instead of the basic fluoberyllate separated at a higher temperature. The method is, however, a tedious one and furnishes a poor yield of the compound (approximetaly 0.2 g. of the basic salt of copper was obtained after heating for 100 hours).

A better result was obtained by the following procedure, particularly for the nickel compound (Guy and Gire, *Compt. rend.*, 1935, **200**, 1213 ; Lamure, *ibid.*, 1945, **220**, 601).

(*b*). Finely powdered pure metallic magnesium was added to an *M*/10 solution of nickel fluoberyllate at 25° in the approximate proportion of 1 : 5 as Mg : Ni. The solution was kept aside for about 7 days. When the powdered magnesium disappeared completely, the product was filtered, washed first with water, then with 60% alcohol, and finally dried in air. The following compounds were isolated in this laboratory.

$CuBeF_4$, $4Cu(OH)_2$, $8H_2O$ was prepared by the method described under (*a*). The solution was made by disolving 14 g. of copper fluoberyllate in 300 c.c. of water. The compound was washed quickly under suction by 60% alcohol, as washing of the precipitate by simple water sometimes resulted in the decomposition or transformation of the basic salts (Aspelund, *Acta Acad. Aboensis. Math. Phys.*, 1933, **7**, 1). The compound was dried by pressing it in the folds of a filter paper. [Found : Cu, 45.83, 45.84 ; Be, 1.37, 1.34. $CuBeF_4$,$4Cu(OH)_2$, $8H_2O$ requires Cu, 46.5 ; Be, 1.32 per cent].

$CuBeF_4$, $4Cu(OH)_2$, $5H_2O$.—When the above compound was dried to a constant weight in air it was converted into the pentahydrate. [Found : Cu, 51.02; Be, 1.35. $CuBeF_4$,$4Cu(OH)_2$, $5H_2O$ requires Cu, 50.53; Be, 1.43 per cent].

$CuBeF_4$, $4Cu(OH)_2$, $3H_2O$.—When the pentahydrate was dried over $CaCl_2$ in a desiccator it changed to the trihydrate. [Found : Cu, 53.8; Be, 1.62. $CuBeF_4$, $4Cu(OH)_2$, $3H_2O$ requires Cu, 53.6; Be, 1.43 per cent].

Though a number of basic sulphates of copper have been described, in the case of the fluoberyllate, however, it has been possible to obtain only one type of basic salt.

$NiBeF_4$, $4Ni(OH)_2$, $5H_2O$ was prepared by the method described under (b). [Found : Ni, 48.32 ; Be, 1.47. $NiBeF_4$, $4Ni(OH)_2$, $5H_2O$ requires Ni, 48.54; Be, 1.49 per cent].

The X'ray diffraction diagrams of this compound has been found to be identical with that of the corresponding sulphate, indicating that they are isomorphous.

$ZnBeF_4$, $3Zn(OH)_2$, $5H_2O$ was prepared by the first method (*a*) *i.e.* by the hydrolysis of a solution of zinc fluoberyllate with the addition of beryllium carbonate at intervals. The solution was made in this case by dissolving 19 g. of $ZnBeF_4$, $7H_2O$ in 200 c.c. of water. (Found : Zn, 48.80 ; Be, 1.65. $ZnBeF_4$, $3Zn(OH)_2$, $5H_2O$ requires Zn, 48.60; Be, 1.67 per cent).

These salts are similar in composition with the corresponding basic sulphates, The number of water molecules attached to them, however, differs in some cases. If during the preparation, the temperature of the solution goes above 80°, the basic fluoride instead of the basic fluoberyllate is formed. The basic fluoberyllates like all other basic salts are perfectly stable under ordinary conditions. At 100° the salts are decomposed. They are practically insoluble in water and alcohol. Even very dilute acids decompose the compounds.

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NEW SUBSTITUTES FOR THE ZIMMERMANN-REINHARDT REAGENT

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Addition of a solution either of sodium acetate or borax to the reaction mixture has been found to yield precisely the same values as obtained by Zimmermann-Reinhardt reagent or by ferrous iron with H_2SO_4.

It is well known that high results are obtained in the permanganametric titrations of iron in hydrochloric acid solution. But addition of Zimmermann-Reinhardt reagent has been known for a long time to give satisfactory results. In a recent communication (*Curr. Sci.*, 1953, **22**, 148) we have shown that addition of a solution either of sodium acetate or of borax to the reaction mixture gives precisely the same values as with either Zimmermann-Reinhardt reagent or with ferrous iron in presence of sulphuric acid. These new reagents have the advantage of easier preparation and a more sharp end-point than with the Zimmermann-Reinhardt reagent. The end-point is a change of colour as sharply as with methyl orange from yellow to orange-red. The colour lasts for not less than one and a half minutes unlike with the Zimmermann-Reinhardt reagent wherein the pink colour does not last more than half a minute nor the end-point is as sharp as either with sodium acetate or with borax.

EXPERIMENTAL

Decinormal solutions of ferrous ammonium sulphate and potassium permanganate were prepared. Zimmermann-Reinhardt reagent was prepared by dissolving 50 g. of $MnSO_4,4H_2O$ (crystals) in 250 c.c. of water and adding a cooled mixture of 100 c.c. of H_2SO_4 (conc.) and 300 c.c. of water, followed by 100 c.c. of syrupy phosphoric acid. Sodium acetate (50 g.) was dissolved in 100 c.c. of water. Borax (16 g.) was dissolved in 400 c.c. of water by heating and subsequent cooling to the laboratory temperature.

Ferrous ammonium sulphate solution (20 c.c.) was taken for each titration. To the aliquot part of the ferrous solution 20 c.c. of $4N$-H_2SO_4 was added and titrated with permanganate solution. The same was repeated using 20 c.c. of $5N$-HCl instead of H_2SO_4. The titration in presence of HCl was repeated with addition of 40 c.c. of Zimmermann-Reinhardt reagent. The same titration was repeated using once 10 c.c. of borax solution and a second time with 6 c.c. of the acetate solution instead of the Zimmermann-Reinhardt reagent. Under identical conditions a second series of experiments was conducted to investigate the effect of adding varying amounts of sodium acetate and borax on the permanganametric titre values for an aliquot quantity of ferrous iron solution. All the chemicals used were of Analar variety. Results obtained are recorded below.

TABLE I

Titre values for 20 ml. of ferrous solution with permanganate.

With 20 ml. of H_2SO_4.	With 40 ml. of HCl.	With 40 ml. of HCl and 40 ml. of Z. R. reagent.	With 40 ml. of HCl and 6 ml. of Na acetate soln.
16.60 ml.	16.80 ml.	16.60 ml.	16.60 ml.

TABLE II

Titre values of permanganate for 20 ml. of ferrous solution.

With 20 ml. of H_2SO_4	With 20 ml. of HCl	With 20 ml. of HCl and 40 ml of Z.R. reagent.	With 20 ml. of HCl and 10 c. c. of borax soln.
16.95 ml.	17.10 ml.	16.95 ml.	16.95 ml.

TABLE III

Effect of varying quantities of sodium acetate on the permanganametric titre value.
Value with the Z.R reagent = 16.60 ml.

Na acetate soln. added (ml)	2	4	6	8	10	12
Titre value of $KMnO_4$ (ml.)	16.70	16.65	16.60	16.60	16.40	16.60

TABLE IV

Effect of varying quantities of borax solution on the permanganametric titre value.
Value with Z.R reagent = 16.95 ml.

Borax soln. added (ml.)	5	10	15	20	25	30	40
Titre value of $KMnO_4$ (ml.)	17.00	16.95	16.95	16.95	16.95	16.95	16 05

TABLE V

20 Ml. of ferrous ammonium sulphate + 20 ml. of $4N$-H_2SO_4 against $KMnO_4$ = 20.35 ml.

20 Ml. of ferrous ammonium sulphate + 20 ml. of $11N$-HCl alone against $KMnO_4$ = 20.6 ml.

20 Ml. of ferrous ammonium sulphate + 20 ml. of $11N$-HCl + 80 ml. of Z.R reagent against $KMnO_4$ = 20 35 ml.

20 Ml. of $11N$-HCl was added in each case below.

Sodium acetate added.	Titre value.	Remarks.
2 g.	20.55 ml.	Intense yellow colour; end-point not sharp.
5	20.40	Do
7	20.40	Do
10	20.35	End-point clearly seen.
12	20.35	Do
15	20.35	Do
18	20.35	Do
20	20.35	Do
25	20.25	Do
30	20.10	Do

TABLE VI

20 Ml. of ferrous solution + 20 ml. of $4N$-H_2SO_4 against $KMnO_4$ = 20.20 ml.

20 Ml. of ferrous solution + 20 ml. of $11N$ HCl + 80 ml. of Z.R. reagent against $KMnO_4$ = 20.20 ml.

20 Ml. of ferrous solution + 20 ml. of $11N$-HCl alone against $KMnO_4$ = 20. 65 ml.

20 Ml. of $11N$-HCl was added in each case below.

Borax added.	Titre value.	Remarks.
1 g.	20.35 ml.	Intense yellow colour; no sharp-end point.
2	20.35	Do
4	20 35	Do
5	20.30	Do
7	20.20	Do
10	20.20	Do
15	20.25	Do

DISCUSSION

It is evident from Table I that sodium acetate serves very well as a substitute for the Zimmermann-Reinhardt reagent.

Table II also shows that a solution of borax also very well serves the same purpose either as the Zimmermann-Reinhardt reagent or sodium acetate.

Table III shows that sodium acetate added in a quantity more than 4 c.c. (2 g.) up to 12 c.c. (6 g.) does not have any effect in changing the titre value of permanganate solution. That means, there is apparently a lower limit of sufficiency for sodium acetate as a reagent. Therefore a correct prescription will be to add enough of sodium acetate (4 to 5 g. approx.) to replace the Zimmermann-Reinhardt reagent.

Table IV shows that addition of borax solution from 10-40 c.c. (0.40-1.60 g.) has no effect on the titre value of permanganate solution required for an aliquot quantity of ferrous solution. A quantity of borax less than 0.4 g. is evidently insufficient. Addition of about 1 g. of borax may as well replace the Zimmermann-Reinhardt reagent.

A comparison of the values with sodium acetate and borax as substitutes for the Zimmermann-Reinhardt reagent shows that though both of them are very much cheaper and save the tedium of preparation of the Zimmermann-Reinhardt reagent and make for an easier, more sharp and lasting end-point, from Tables III-IV it is amply evident that a much smaller quantity of borax does serve the purpose equally well and therefore borax gets a better claim as a substitute for the Zimmermann-Reinhardt reagent than sodium acetate.

Tables V and VI record results obtained with sodium acetate and borax respectively in presence of 20 ml. of 11*N*-HCl, that is under conditions of presence of extremely concentrated HCl, 10-20 g. of sodium acetate and a narrow range of only 7-10 g. of borax are seen to be useful as good substitutes.

Mechanism of Action of the Zimmermann-Reinhardt Reagent

Kessler (*Pogg. Ann.*, 1863, **118**, 779; **119**, 225) and Zimmermann (*Ber.*, 1881, **14**, 779; *Annalen*, 1882, **213**, 302) showed that when permanganate was run into a solution containing ferrous ions and hydrochloric acid and manganous sulphate, the ferrous iron was quantitatively oxidised to ferric iron without any evolution of chlorine. Reinhardt (*Chem. Ztg.*, 1889, **13**, 323) suggested the use of phosphoric acid for keeping down the concentration of ferric ions. Manchot (*Annalen*, 1902, **325**, 105) showed that iron like manganese had a tendency to form unstable compounds as primary oxidation products, giving up its excess charge to the manganous ions rather than to the chloride ions, provided that sufficient manganous ions were present. Zimmermann also suggested a similar explanation. Allmand and Franklin (*J. Chem. Soc.*, 1930, 2073) have shown that addition of manganous chloride to an air-saturated solution of hydrochloric acid causes a 20% diminution in the velocity of the oxidation of the acid. The mechanism of the action of manganous sulphate may be ascribed to its retarding the induced oxidation of hydrochloric acid in presence of ferrous chloride.

The oxidation-reduction potentials of the system should be considered for a better understanding of the problem. The E_0 of Pt, Cl^-, $Cl_2(g)$ is -1.3594 (Lewis and Rupert,

J. Amer. Chem. Soc., 1911, **33**, 299); E_0 of Mn^{2+}, MnO_4^-, H^+ is -1.520 (Glasstone, "Introduction to Electrochemistry", Van Nostrand Co., 1947, p. 279); E_0 of Fe^{2+}, Fe^{3+} is -0.783 (Maitland, *Z. Elektrochem.*, 1906, **12**, 263). The theoretical oxidation potential required to give a quantitative oxidation of ferrous ions to ferric is not sufficiently high to cause an appreciable oxidation of chloride ions. The equilibrium between MnO_4^- and Mn^{2+} ions adjusts itself very slowly so that near the end of the titration, the oxidation potential momentarily exceeds the theoretical value after the addition of each drop of permanganate solution. As a result, a slight oxidation of the chloride ions does occur unless precaution is taken.

It has been found in our laboratory that without the addition of Zimmermann-Reinhardt or any other reagent, there is a fluctuation of the oxidation potential during the permanganate titration of ferrous iron, as could be seen in the unsteadiness of the pointer in the Cambridge potentiometer. Remarkable steadiness of oxidation-reduction potential is the most important observation made by us on the addition of either the Zimmarmann-Reinhardt reagent or sodium acetate.

The reason of the addition of phosphoric acid, advocated by Reinhardt, is that PO_4^{3-} ions give complexes by combination with Fe^{3+} ions at the same time allowing oxidation of Fe^{2+} ions by permanganate at a sufficiently low potential quite insufficient to effect the oxidation of the chloride ions.

The action of sodium acetate or borax as substitutes for the Zimmermann-Reinhardt reagent could perhaps be visualised as due to the liberation of the corresponding weak acids whereby a proportional amount of hydrochloric acid is removed from the system and the effect of the latter is attenuated.

Sutton ("A Systematic Hand-book of Volumetric Analysis", 1924, J. and A. Churchill, London, pp. 130, 238) quotes the efficacious use of ammonium sulphate as a substitute for the Zimmermann-Reinhardt reagent. Though we could not confirm the above claim we found potassium sulphate to be effective. The phosphate ion could as well be replaced by the fluoride ion which serves the same purpose of reducing the oxidation-reduction potential of the system by forming complexes with ferric ions. Under certain conditions we have found that a combination of potassium sulphate and potassium fluoride in specified proportions serves as a substitute for the Zimmermann-Reinhardt reagent. Details of these investigations have been communicated elsewhere.

The concentration of the acid has an important role in contributing towards the oxidation-reduction potential of the system. The Zimmermann-Reinhardt reagent functions properly only in presence of a high concentration of sulphuric acid.

On the whole, the addition of borax or sodium acetate increases the p_H of the solution; the oxidation potential of $KMnO_4$ decreases with increase of p_H and falls below that of Cl°-Cl' system but sufficiently higher than that of $Fe^{3+}-Fe^{2+}$ system. The purpose of phosphoric acid is served by fluoride ion.

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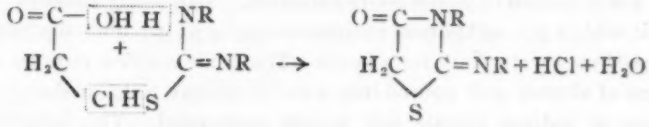
STUDIES ON 3-*o*-TOLYL-2-*o*-TOLYLIMINO-4-THIAZOLIDONE

By Prithwi Nath Bhargava and Chuni Lal Kaul

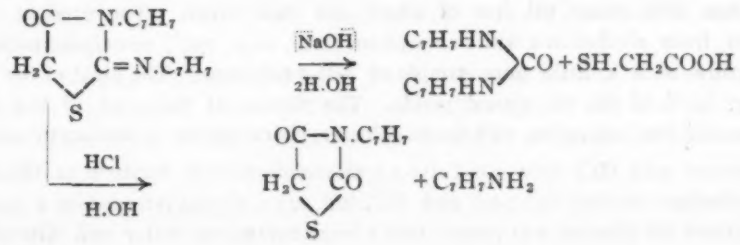
3-*o*-Tolyl-2-*o*-tolylimino-4-thiazolidone has been synthesised from *s*-di-*o*-tolylthiourea and monochloroacetic acid and the characteristics of the compound have been studied.

Desai, Hunter and Koppar (*Rec. trav. chim.*, 1935, **54**, 118) prepared 3-phenyl-2-phenylimino-4-thiazolidone; Klare, Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) studied the conditions for the preparation of this compound by condensing diphenylthioure with monochloroacetic acid in the presence of anhydrous sodium acetate in absolute alcohol by means of the general reaction:



Similar compounds with aryl groups, such as anisyl, phenetyl, α-naphthyl and β-naphthyl, have been synthesised by Bhargava (*ibid.*, 1951, **73**, 2353). This reaction has now been made use of in the preparation of 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone. Here *s*-di-*o*-tolylthiourea has been condensed with monochloroacetic acid in absolute alcohol in the presence of anhydrous sodium acetate.

Reaction conditions on the formation of 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone show that the highest yield is obtained when the amount of monochloroacetic acid is slightly in excess over the required molar quantity and the time of reflux is about 3 hours. The secondary formation of 3-*o*-tolyl-2 : 4 thiazolidone has been successfully suppressed by the addition of a sufficient quantity of anhydrous sodium acetate, which removes HCl *in situ*. The structure of 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone is quite apparent from its method of preparation. The compound possesses a reactive methylene group and a sulphur atom as members of the ring system. Due to the presence of the reactive methylene group, the thiazolidone condenses at position-5 with various aldehydes and ketones affording 5-substituted-4-thiazolidones. Its decomposition into *s*-di-*o*-tolylurea and thiolacetic acid with concentrated alcoholic NaOH and hydrolysis with acid into *o*-toluidine and 3-*o*-tolyl-2 : 4-thiazolidione clearly confirm the structure of this compound.



Finally, on oxidation with chromic anhydride according to the method of preparation of methyl ester of benzylpenicillin sulphone (Merck Monograph, 56, p. 7; 59, p. 21), 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone sulphone has been obtained, which is neutral, odourless and resistant to reducing agents.

EXPERIMENTAL

3-o-*Tolyl*-2-o-*tolylimino*-4-*thiazolidone*.—*s*-Di-*o*-tolylthiourea (5.12 g.), monochloroacetic acid (2 g.), anhydrous sodium acetate (4.92 g.) and absolute alcohol (50 c.c.) were refluxed on a water-bath for 2 hours. The crude reaction mixture was distilled to remove excess of alcohol and poured into water to remove NaCl produced in the reaction and the excess of sodium acetate left behind unchanged. The solution was filtered and the residue dried and crystallised from alcohol in yellow leaflets, m.p. 152°. (Found: S, 10.92. $C_{17}H_{16}ON_2S$ requires S, 10.81 per cent). It is readily soluble in benzene but soluble in alcohol only on boiling.

Several experiments under different experimental conditions were performed. Table I shows the effect of the reaction conditions on the yield of the thiazolidone.

TABLE I

$(C_7H_7NH)_2CS$.	$ClCH_2COOH$.	Anhydrous Na acetate.	Absolute. alcohol.	Time of reflux.	Yield.		%S.
5.12 g.	2.0 g.	5.0 c.c.	50 c.c.	2.0 hrs.	4.16 g.	70.2%	11.02
5.12	2.8	5.0	50	2.0	5.10	86.2	11.08
5.12	3.5	5.0	50	2.0	5.15	87.0	10.98
2.56	1.5	3.5	25	2.5	2.62	88.4	...
2.56	1.5	3.5	25	3.0	2.70	91.2	11.04
2.56	1.7	4.0	30	3.5	2.61	88.2	10.92
2.56	1.5	3.5	25	4.0	2.57	87.0	11.11
2.56	1.5	3.5	25	5.0	2.51	85.0	11.05

Decomposition with NaOH *into* s-*Di*-o-*tolylurea*.—Thiazolidone (2.46 g.) was dissolved in boiling absolute alcohol (25 c. c.) and to this alcoholic *N*-NaOH (40 c.c.) was added. The reaction mixture was refluxed on a water-bath for 3 hours. It was poured into a large volume of cold water and filtered. The residue was washed several times with water till free of alkali and then dried. The product was recrystallised from alcohol in a white amorphous form, m.p. 250°, remaining undepressed on admixture with a little pure sample of *s*-di-*o*-tolylurea. The yield of the product was 2.16 g. (94% of the theoretical yield). The filtrate at the end of the reaction gave a greenish blue coloration with ferric chloride, characteristic of thiolacetic acid.

Hydrolysis with HCl *into* 3-o-*Tolyl*-2:4 *thiazolidione*.—A mixture of thiazolidone (5.2 g.), absolute alcohol (20 c.c.) and HCl (dil., 25 c.c.) was refluxed on a water-bath for 4 hours and the mixture was poured into a large volume of water and filtered. The

precipitate was repeatedly washed with water to remove the acid completely. The compound was dried and crystallised from benzene in a yellow amorphous form, m.p. 154°. (Found : S, 15.61. $C_{16}H_{9}O_{2}NS$ requires S, 15.46 per cent).

The presence of *o*-toluidine hydrochloride in the filtrate was confirmed by the preparation of its azo-*β*-naphthol derivative, m.p. 128°.

3-*o*-*Tolyl*-2-*o*-*toiylimino*-5-*benzal*-4-*thiazolidone*.—Thiazolidone (3 g.), benzaldehyde (1.5 g.), benzene (20 c.c.) and pyridine (4 drops) were heated under reflux in a paraffin bath at 150°-160° for 4 hours. The excess of benzene was removed by heating on a water-bath. The residue was washed with HCl (dil.) and hot water and finally with alcohol, and filtered. From the alcoholic solution a resinous product was obtained, which solidified on standing, yielding a brown amorphous powder, m.p. 95°. (Found : S, 8.22. $C_{24}H_{20}ON_{2}S$ requires S, 8.33 per cent).

Similarly 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone was condensed with *p*-dimethylaminobenzaldehyde, anisaldehyde, acetone and *p*-chloroacetophenone yielding respectively the corresponding 5-substituted-4-thiazolidones. Table II summarises the results.

TABLE II

Solvent : benzene.

Aldehyde or ketone.	Condensing agent.	M.P. of 5-substituted derivative.	Percentage of sulphur. Found.	Calc.
p-Dimethylamino-benzaldehyde	Pyridine	65°	7.86	7.50
Anisaldehyde	Pyridine or piperidine	131°	...	...
*Acetone	Pyridine	141°	9.63	9.52
p-Chloroacetophenone	Do	147°	7.32	7.40

* In case of acetone, acetone was used as the solvent.

3-*o*-*Tolyl*-2-*o*-*tolylimino*-4-*thiazolidone Sulphone*.—Thiazolidone (2 g.) was dissolved in acetone (30 c.c.) and to this chromic acid anhydride (4 g.) was slowly added little by little at a time within 1 hour. The solution was heated on a water-bath for 1 hour and the excess of acetone was distilled off. The product was poured into about 400 c.c. of ice-cold water containing sufficient crushed ice. The precipitate obtained was repeatedly washed with water, dried, treated with rectified spirit and filtered. The filtrate on evaporation gave a greyish white, neutral, odourless, amorphous powder, which on recrystallisation from benzene melted at 134°. It is readily soluble in CCl_4 and resistant to reducing agents. From analytical data which correspond to addition of two atoms of oxygen and usual properties, the compound is ascribed to be a sulphone. (Found : C, 62.08 ; H, 4.85 ; N, 8.5 ; S, 9.83. $C_{17}H_{16}O_{3}N_{2}S$ requires C, 62.19 ; H, 4.87 ; N, 8.53 ; S, 9.76 per cent).

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HALOGENATION OF ETHYL β-ARYLAMINO-αβ-UNSATURATED ESTERS: BROMINATION OF ETHYL ARYLAMINOMETHYLENE-ACETOACETATES AND -MALONATES AND ETHYL β-ARYLAMINO-β-CARBETHOXY-ACRYLATES

By R. K. Mapara and C. M. Desai

Bromination of several ethyl arylaminomethylene-acetoacetates, -malonates and ethyl β-arylamino-β-carbethoxyacrylates has been investigated. Except in the case of ethyl *m*-nitroanilinomethylene-acetoacetate and -malonate, bromine enters the side-chain as well as the nucleus of all other acrylates, forming αβ-dibromo derivatives containing two or three bromine atoms in the benzene ring. The compounds are fairly stable in air but are affected by moisture.

αβ-Dibromo derivatives of olefinic acids such as γ-methoxycrotonic acid, *p*-ethoxybenzalpyruvic acid and ethyl αβ-dichloro-β-ethoxypropionate have been reported to be unstable and sensitive to moisture (Owen and Sultanbawa, *J. Chem. Soc.*, 1949, 3105; Reimer and Morrison, *J. Amer. Chem. Soc.*, 1941, **63**, 236; Croxall and Fegley, *ibid.*, 1950, **72**, 2888). Further, the elimination of halogen acid from the αβ-dihalogen derivatives could be easily effected by treatment with either alkali or organic bases, and unsaturated α-halogen acids could be obtained (Owen and Sultanbawa, *loc. cit.* Croxall and Fegley, *loc. cit.*).

Very little work seems to have been done on the halogenation of ethyl β-arylamino-αβ-unsaturated esters. Dains (*Ber.*, 1902, **35**, 2510) carried out the bromination of ethyl anilinomethylene-cyanoacetate in glacial acetic acid and obtained a monobromo derivative which was later proved to be ethyl α-cyano-β-*p*-bromoanilinoacrylate by Dains and Griffin (*J. Amer. Chem. Soc.*, 1913, **35**, 963).

Dains, Brien and Johnson (*ibid.*, 1916, **38**, 1510) suggested that the aminomethylene compounds containing the grouping $>C:CH.NHR$ reacted also in the tautomeric form $>CH.CH:NR$. The dibromide obtained from the latter form may under the influence of solvents either lose its bromine entirely or undergo rearrangement, yielding a monosubstitution product and hydrogen bromide.

The present work indicates that when bromination of ethyl arylaminomethylene-acetoacetates, -malonates and ethyl β-arylamino-β-carbethoxyacrylates is carried out with 3 to 4 moles of bromine per mole of anil in dry chloroform, bromine enters the side-chain of all acrylates forming αβ-dibromo derivatives. Further, it also enters the nucleus in all the cases except *m*-nitroanilinoacrylates.

The aqueous solution of each brominated product is strongly acidic. It is slowly decomposed by cold water but readily by hot water and alkali, with the separation of a bromoamine or the unsubstituted amine. With silver nitrate its aqueous solution gives a precipitate of silver bromide. The amines obtained by the alkaline decomposition of the corresponding brominated anils were found to be the same in the case of all the three esters.

The bromine in the side-chain was estimated in all the brominated products by Volhard's method after alkaline decomposition. The side-chain was thus found to contain two bromine atoms in all the cases. The structure of the dibromide is represented below :

$$\begin{matrix} R_1 \\ \diagup \\ \quad > C{:}\ CH.NH.R \\ \diagdown \\ R_2 \end{matrix} + Br_2 = \begin{matrix} R_1 \\ \diagup \\ \quad > CBr-CHBr.NHR \\ \diagdown \\ R_2 \end{matrix}$$

$$\begin{matrix} C_2H_5OOC \\ \diagup \\ \quad > C{:}\ C(COOC_2H_5).NHR \\ \diagdown \\ H \end{matrix} + Br_2 = \begin{matrix} C_2H_5OOC \\ \diagup \\ \quad > CBr-BrC(COOC_2H_5).NHR \\ \diagdown \\ H \end{matrix}$$

EXPERIMENTAL

Ethyl arylaminomethylene-acetoacetates were prepared by heating equimolecular quantities of ethyl ethoxymethylene-acetoacetate and various aromatic amines in a steam-bath. Ethyl arylaminomethylene-malonates were prepared by the method of Duffin and Kendall (*J. Chem. Soc.*, 1948, 893). Ethyl β-arylamino-β-carbethoxy-acrylates were prepared by the method of Surrey and Hammer (*J. Amer. Chem. Soc.*, 1946, **68**, 113). All the acrylates were purified by washing with 1 *N*-HCl, then with 10% solution of sodium bicarbonate and finally with water.

Ethyl αβ-Dibromo-2 : 4 : 6-tribromoanilinomethylene-acetoacetate.— Ethyl anilino-methylene-acetoacetate (5 g.) was dissolved in cold dry chloroform (15 c.c.). Bromine (13.7 g.), dissolved in chloroform (15 c.c.), was gradually added to it within 20 minutes. No solid separated in the beginning. However, after half an hour white needle-shaped crystals separated. On standing, the amount of the product slowly increased. The mixture was therefore left overnight. The crystals were filtered, washed repeatedly with chloroform to remove adhering bromine and finally with petroleum ether, yield 4.6 g. (34%). The bromo derivative began to blacken at 140° and melted at 197° (decomp.). [Found : Br (in the side-chain by Volhard's method), 25.0. $C_{13}H_{12}O_2NBr_5$ requires Br, 25.4 per cent]. The result indicates two bromine atoms in the side-chain.

The brominated product was stable in dry air, but it was affected by moisture. It was slowly decomposed by cold water but rapidly by boiling water and alkali affording 2 : 4: 6-tribromoaniline (m.p. 119°). Its mixed melting point with an authentic specimen of 2: 4: 6-tribromoaniline was not depressed. All other anils were brominated and treated in the same manner. The experimental details are summarised in Table I.

TABLE I

Bromination products.

		*Bromine added.	Yield.	Crystalline form.	M.P. (with decomp.).	Decomposition product.	Formula.	% Br in the side-chain. Found.	Calc.
				With ethyl arylaminomethylene-acetoacetates.					
(1)	Unsubstituted	4 moles	34%	White needles	197°	2 :4 :6-Tribromo-aniline	$C_{13}H_{12}O_3NBr_3$	25.0	25.4
(2)	*m*-Toluidino-	4	39	,,	186°	2 :4 :6-Tribromo-*m*-tolnidine	$C_{14}H_{14}O_3NBr_3$	24.3	24 8
(3)	*p*-Anisidino-	3	40	,,	225°	3 :5-Dibromo-*p*-anisidine	$C_{14}H_{15}O_4NBr_4$	27.3	27.5
(4)	*o*-Phenetidino-	3	54	,,	215°	3 :5-Dibromo-*o*-phenetidine	$C_{15}H_{17}O_4NBr_4$	26.2	26.9
(5)	*p*-Chloroanilino-	3	29	,,	224°	2 :6-Dibromo-*p*-chloroaniline	$C_{12}H_{12}O_3NClBr_4$	27.1	27.3
(6)	*m*-Nitroanilino-	4	44	Yellow needles	244°	*m*-Nitroaniline	$C_{13}H_{14}O_5N_2Br_2$	37.2	36.5
				With Ethyl arylaminomethylene-malonates					
(1)	Unsubstituted	4	37%	White needles	210°	2 :4 :6-Tribromo-aniline	$C_{14}H_{14}O_4NBr_3$	24.9	24.2
(2)	*m*-Toluidino-	4	30	,,	187°	2 :4 :6-Tribromo-*m*-toluidine	$C_{15}H_{16}O_4NBr_3$	24.1	23.7
(3)	*p*-Anisidino-	3	27	,,	209°	3 :5-Dibromo-*p*-anisidine	$C_{15}H_{17}O_5NBr_4$	26.6	26.2
(4)	*o*-Phenetidino-	3	82	,,	217°	3 :5-Dibromo-*o*-phenetidine	$C_{16}H_{19}O_5NBr_4$	24.9	25.6
(5)	*p*-Chloroanilino-	3	30	White prisms	235°	2 :6-Dibromo-*p*-chloroaniline	$C_{14}H_{14}O_4NClBr_4$	26.4	26.0
(6)	*m*-Nitroanjlino-	4	40	Yellow leaflets	215°	*m*-Nitroaniline	$C_{14}H_{16}O_6N_2Br_2$	34.7	34.2
				With ethyl β-arylamino-β-carbethoxyacrylates.					
(1)	Unsubstituted	4	55%	White needles	194°	2 :4 :6-Tribromo-aniline	$C_{14}H_{14}O_4NBr_3$	24.7	24.2
(2)	*m*-Toluidino-	4	59	,,	179°	2 :4 :6 Tribromo-*m* tolnidine	$C_{15}H_{16}O_4NBr_3$	23.1	23.7
(3)	*p*-Anisidino-	3	68	,,	223°	3 :5 Dibromo-*p* anisidine	$C_{15}H_{17}O_5NBr_4$	25.7	26.2
(4)	*o*-Phenetidino-	3	42	,,	212°	3 :5-Dibromo-*o* phenetidine	$C_{16}H_{19}O_5NBr_4$	24.8	25.6
(5)	*p*-Chloroanilino-	3	54	,,	188°	2 :6-Dibromo-*p*-chloroaniline	$C_{14}H_{11}O_4NClBr_4$	25.2	26.0

*Proportion per mole of the anil.

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THIAZOLE DERIVATIVES AS POSSIBLE FUNGICIDES. PART I. 2-SUBSTITUTED-AMINO-4 : 5-DIMETHYLTHIAZOLES

By Nabin Kishore Das, G. N. Mohapatra and M. K. Rout

The preparation of thirteen new 2-substituted-amino-4 :5-dimethylthiazoles and their acetoxy-mercuri derivatives is described. The mercurated thiazoles have been found to be very effective as fungicides.

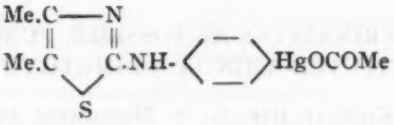
In course of our investigations on the preparation and uses of thiazoles and their derivatives, it was considered w rthwhile to examine their fungicidal properties. Other types of thiazole compounds have been al·eady reported by others to possess fungicidal activity. Asterol dihydrochloride, which is 2-diethylamino-(β-diethylamino-ethoxy)-benzothiazole, is commercially available as a potent fungistatic agent. Mercaptobenzothiazole is not only fungicidal in action, as has been shown by Marsh (*Ann. Appl. Biol.*, 1938, **25**, 583), but also accelerates the fungicidal activity of sulphur (Dimond and Horsfall, *Science*, 1943, **97**, 144; *Phytopath.*, 1945, **34**, 136). It is also interesting to note that the compounds studied in the present investigation contain in their ring structure the grouping N-C-S, which is present in known fungic des like tetramethylthiuram disulphide (Tisdale and Williams, U.S. P. 972, 961; Marsh, *J. Hort. Sci.*, 1938, **7**, 237), thiourea, thioacetamide, thiocarbanilide and thiosemicarbazide (Beureart, "Insecticides, Fungicides and Weed Killer"; Goldsworthy, *Phytopath.*, 1942, **32**, 498). Investigation in this direction therefore appeared to be of interest.

There was also another aim in view in preparing these compounds. Dimond and Horsfall (*loc. cit.*) have also reported that the action of sulphur in rubber and as a fungicide is comparable. Hence a systematic study of the fungicidal activities of the compounds prepared here would also serve as screening of these compounds for vulcanisation action.

The thiazole compounds studied herein are thirteen in number, mostly new 2-substituted-amino-4 : 5-dimethylthiazoles, prepared by the modified method already reported by Rout and Pujari (*J. Amer. Chem. Soc.*, 1953, **75**, 4057). The bactericidal activities of these compounds have also been assayed. These compounds are characterised by the presence of two methyl groups in 4- and 5-positions of the thiazole nucleus, and as such differ from other thiazole compounds, bactericidal activities of which have already been studied in earlier investigations. The effect of these substituents can therefore be simultaneously ascertained.

All the 13 thiazolylamines have been mercurated. The usefulness of mercury for combating the attacks of fungii on plants, on animals and on wool fabrics is quite well known. Organo-mercurials are favoured by some for controlling diseases like Apple Scab which is caused by the fungus *Venturia ineaqualis*. A 2½% solution of phenylmercuric acetate is considered quite promising as a fungicide (*Discovery*, 1954, **15**, 32). Mercuration is therefore expected to lead to discovery of more effective fungicides.

On the basis of our earlier findings (Pujari and Rout, this *Journal*, 1954, **31**, 357; *loc. cit.*) the following structure has been assigned to the mercurated derivative.



The method of preparation of one of the thiazolylamines has been illustrated in the Experimental.

EXPERIMENTAL

2-Phenylamino-4:5-dimethylthiazole. — Phenylthiourea (5.06 g.), ethylmethyl ketone (0.9 g.) and iodine (4.5 g.) were refluxed on a water-bath for 24 hours and for 6 to 8 hours without the use of condenser. The coloured crude reaction product was kept in contact with ether for 48 hours with occasional stirring. After decanting off the ether, dilute sodium thiosulphate solution was added with vigorous stirring. This removed effectively the remaining iodine. The product was boiled with water to remove unchanged thiourea. A gum was obtained which did not solidify by treatment with concentrated ammonia. Its picrate was prepared and was treated with lithium hydroxide and then vigorously shaken. On extraction with ether and its subsequent evaporation the solid thiazole was obtained.

Mercuration of Thiazoles.—The thiazole compound (1 mole) was dissolved in alcohol-acetic acid solution. A solution of mercuric acetate (1.3 mole) in water, acidified with acetic acid, was then added. Precipitate appeared after sometime. The reaction mixture was kept overnight, filtered and then purified by repeated washing with hot water and very dilute acetic acid.

Bactericidal Tests.—The Rideal-Walker drop dilution method was used for the comparative antibacterial activity. The bactericidal activity was measured in terms of maximum effective dilution (M.E.D.) of the mercurials at 10 minutes' contact, the test organisms used being twenty four hours' cultures of *E. Coli* and *Staphylococcus aureus*. The unmercurated thiazoles exhibited activity in maximum dilutions of 1:1,000, while the mercurated thiazoles were active in dilutions up to 1:75,000.

Fungicidal Tests.—For fungicidal assay, the method of Montgomery and Moore (*J. Pomol & Hort. Sci.*, 1938, **25**, 253) with silght modification has been used. *Alternaria Polanduii*, Ayyangar was used as the fungus indicator. All the 26 thiazoles (13 unmercurated and the rest mercurated) have been tested. The unmercuratad thiazoles completely inhibited spore germination at a concentration of 100 parts per million (p.p.m.). At 250 p.p.m., the percentage of inhibition was only 25 to 30%. The mercurated thiazoles were, however, more powerful, being 100% effective in inhibiting the spore germination of the fungus even at concentration of 2 p.p.m. Details of the fungicidal tests will be published elsewhere.

The properties and analytical data of the thiazoles are shown in Table I and those of mercurated thiazoles in Table II.

TABLE I

4 : 5-Dimethyl-2-arylaminothiazoles.

Compd. No.	Nature of the aryl group.	M.P.	Yield.	% Sulphur. Found.	Calc.	M.P. of the picrates.
1	Phenyl	165°	65 %	15.10	15.6	180°
2	*o*-Tolyl	168°	51	14.56	14.9	178°
3	*p*-Tolyl	167°	50	14.29	14.6	195°
4	*o*-Chlorophenyl	120°	50	13.40	13.4	115°
5	*m*-Chlorophenyl	176°	56	13.12	13.4	212°
6	*p*-Chlorophenyl	104°	53	13.21 (N, 11.32	13.4 11.7)	108°
7	*o*-Carboxyphenyl	215°	Very low	—	12.9	235°
8	*m*-Carboxyphenyl	175°	44	12.4	12.9	250°
9	*p*-Carboxyphenyl	225°	43	12.3	12.9	224°
10	α-Naphthyl	85°	65	12.4 (N, 10.85	12.6 11.02)	196°
11	β Naphthyl	150°	65	12.30	12.6	264°
12	*m*-Nitrophenyl	182°	55	13.60	13.5	185°
13	*p*-Nitrophenyl	180°	58	13.38	13.5	176°

TABLE II

2-(Acetoxymercuri-arylamino)-4 : 5-dimethylthiazoles.

Compd. No.	Nature of aryl substituent in the arylamino group.	M.P.	Yield.	% Mercury. Found.	Calc.
1	Phenyl	175°	75 %	43.4	43.2
2	*o*-Tolyl	230°	69	42.4	42.0
3	*p*-Tolyl	210°	67	42.8	42.0
4	*o*-Chlorophenyl	165°	73	40.9	41.1
5	*m*-Chlorophenyl	135°	71	41.15	41.1
6	*p*-Chlorophenyl	145°	74	41.7	41.1
7	*o*-Carboxyphenyl	245°	65	39.6	39.5
8	*m*-Carboxyphenyl	225°	63	39.8	39.5
9	*p*-Carboxyphenyl	240°	60	39.9	39 5
10	α-Naphthyl	260°	80	38.7	39.03
11	β-Naphthyl	257°	82	40.1	39.03
12	*m*-Nitrophenyl	215°	75	39.1	39.5
13	*p*-Nitrophenyl	> 300	73	39.8	39.5

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ACTION OF HYDROGEN SULPHIDE ON POTASSIUM METAPERIODATE

By Kundan Lal and Gurdas Singh

The action of H_2S on KIO_4 may be represented by the equations.

$$6KIO_4 + 13H_2S = 2K_2SO_4 + KIO_3 + KI + 2I_2 + 13H_2O + 11S \quad \text{... (a)}$$

$$KIO_3 + KI + H_2O + 2S = K_2SO_4 + H_2S + I_2 \quad \text{... ... ... (b)}$$

$$3I_2 + 3H_2S = 6HI + 3S \quad \text{... ... ... (c)}$$

Addition of a, b and c gives

$$6KIO_4 + 15H_2S = 3K_2SO_4 + 6HI + 12H_2O + 12S \quad \text{(d)}$$

or

$$2KIO_4 + 5H_2S = K_2SO_4 + 2HI + 4H_2O + 4S$$

The final equation represents the reaction in the final stage and H_2S reacts with I_2 to form HI only when IO_3', formed during the reaction, is completely consumed.

Reaction of H_2S on different oxidising agents such as chromates and permanganates has already been studied by Dunnicliff and Nijhawan, (*J. Chem Soc.*, 1926, 1), Dunnicliff and Soni (*J. Phys. Chem.*, 1929, **33**, 81), Dunnicliff and Kotwani (*ibid.*, 1931, **35**, 3214) and on manganese dioxide by Lal (this *Journal*, 1952, **21**, 934). Bahl and Singh studied its action on aqueous solution of paraperiodic acid (*ibid.*, 1939, **16**, 339). The present work deals with the action of hydrogen sulphide on potassium metaperiodate.

Experimental

Hydrogen sulphide was prepared and purified as described by Dunnicliff and Kotwani (*loc. cit.*). Its aqueous solution was prepared by passing purified gas through a coloured bottle, filled up to the brim with distilled water and surrounded by ice water, till it was saturated. Potassium metaperiodate, required for this purpose, was prepared by passing chlorine gas through a boiling solution of KOH in presence of iodine (Bahl and Singh, this *Journal*, 1940, **17**, 167). Due to its low solubility in water, 3.0 g. of it was dissolved in one litre of distilled water. Hydrogen sulphide water, thus prepared, was added dropwise to each of the two beakers, containing 150 c.c. of 0.3% KIO_4 solution and surrounded by ice water until the iodine liberated was completely exhausted ; 78.1 c.c. of hydrogen sulphide water was required in each experiment. The resulting solution was milky in colour. The volume in each case was made up to 250 c.c. with distilled water (Expt. No. 4).

On qualitative analysis this solution was found to contain potassium iodide, potassium sulphate and hydriodic acid in addition to some sulphur. The solution was acidic in reaction.

With the varying amounts of hydrogen sulphide water as 15, 30, 50, 100 and 120 c.c., different stages of the reaction were studied exactly in the similar way. All the experiments were performed in duplicate. The results of the various quantitative estimations are recorded in Table I. In the experiment, when 15 c.c. of hydrogen sulphide water was added, the resulting solution was found to contain potassium iodate, potassium sulphate and free iodine along with some unchanged potassium metaperiodate. In experiments No. 2 and 3, when 30 c.c. and 50 c.c. of hydrogen sulphide

water were added respectively, the products of reaction were found to be the same excepting the formation of some potassium iodide and absence of any unchanged potassium metaperiodate. So far the solution was observed to be neutral in all the experiments. In experiments No. 4 and 5, both potassium iodate and free iodine were found to be absent. Due to the formation of hydriodic acid the solution in experiment No. 4 and those afterwards were found to be acidic. In the final stage (Expt. No. 6) potassium sulphate and hydrochloric acid besides sulphur were the only products of reaction. Presence of some unchanged hydrogen sulphide was also noticed in the final stage of the reaction. The various products of reaction were estimated as shown below.

Metaperiodate (unreacted) was estimated by titrating the iodine liberated, when potassium iodide solution was added to a known volume of the resulting solution in presence of a requisite quantity of a saturated solution of sodium bicarbonate, against a standard solution of As_2O_3 (Scott, "Standard Methods of Chemical Analysis", p. 458).

Iodate content was determined by estimating IO_4' and IO_3' together by treating the iodine, liberated by the addition of potassium iodide solution and excess of sulphuric acid, against sodium thiosulphate solution and then subtracting from this the value corresponding to IO_4', as obtained by the previous process (Partington and Bahl, *J. Chem. Soc.*, 1934, 1087).

Iodine was estimated by extracting it with CCl_4 and then titrating against sodium thiosulphate solution in presence of a strong solution of potassium iodide (Bahl and Singh, *loc. cit.*).

Iodide was estimated by titrating a known volume of the solution against potassium iodate solution in presence of strong hydrochloric acid and some chloroform (IO_3', when already present as one of the products of reaction, was taken into account for calculating iodide). From this, by subtracting the value due to hydriodic acid, that due to KI was calculated (Scott, *loc. cit.*, p. 455). Hydriodic acid was estimated by direct titration against a standard alkali solution.

Sulphate was estimated as barium sulphate in presence of an excess of hydrochloric acid (Bahl and Singh, *loc. cit.*).

TABLE I

Total potassium added = 0.0765 g. Total iodine added = 0.2484 g.
KIO_4 solution used = 150 c.c. (0.3%).

Expt. No.	H_2S water added.	IO_4'.	IO_3'.	I'.	I_2.	SO_4''.	HI.	Total I_2 (from Col. 3-6 & 8).	Total K (from Col. 3-5 & 7).
1.	15.0 c.c.	0.1198 g. 0.1164	0.1320 g. 0.1331	Nil	0 0736 g. 0.0748	0.0286 g. 0.0294	Nil	0.2490 g. 0.2488	0.0772g 0.0775
2.	30.0	Nil	0.1416 0.1430	0.0023 g. 0.0022	0 1431 0.1425	0.0551 0.0549	Nil	0.2485 0.2484	0.0771 0.0773
3.	50.0	Nil	0.0606 0.0612	0.0437 0.0437	0.1610 0.1602	0.0608 0.0615	Nil	0.2487 0.2483	0.0765 0.0773
4.	78.1	Nil	Nil	0.0641 0.0641	Nil	0.0703 0.0707	0.1852 g. 0.1860	0.2479 0.2486	0.0770 0.0773
5.	100.0	Nil	Nil	0.0343 0.0343	Nil	0.0805 0.0808	0.2153 0.2153	0.2479 0.2479	0.0762 0.0764
6.	120.0	Nil	Nil	Nil	Nil	0.0948 0.0943	0.2501 0.2506	0.2481 0.2486	0.0772 0.0768

DISCUSSION

Analytical results in Table I reveal that in the first experiment metaperiodate is not completely reduced, nor any iodide is formed in this stage of the reaction. In the second experiment IO_4' is completely consumed and potassium iodide in small quantity is formed. There occurs an increase in IO_3', I_2 and SO_4'' contents. In the third experiment IO_3' content decreases but the values of I', I_2 and SO_4'' increase. After this stage IO_3' and I_2 are found to be absent amongst the products of reaction. The analytical results of this stage seem to be in agreement with the equation

$$6KIO_4 + 13H_2S = 2K_2SO_4 + KIO_3 + KI + 13H_2O + 11S \quad \ldots (1)$$

In the next stage (Expt. No. 4) there remains no free iodine in the resulting solution. IO_3' content is also found to be absent. In this as well as the stages afterwards the solution behaves acidic. This may be due to the formation of hydriodic acid, resulting from the action of additional hydrogen sulphide on iodine, liberated according to the equation

$$I_2 + H_2S = 2HI + S \quad \ldots \quad \ldots \quad \ldots (2)$$

It further seems that the presence of IO_3' does not allow this reaction to proceed. Potassium iodide, being maximum here, decreases in the next stages. In experiment No. 5 KI content decreases, whereas the SO_4'' and HI contents both increase. In the final stage (Expt. No. 6) the reaction affords the formation of SO_4'' and HI only. Whole of the potassium is accounted for as SO_4'' and iodine as HI. Presence of some unchanged hydrogen sulphide was also detected in the final stage of the reaction This was removed by shaking whole of the solution with $CdCO_3$ suspended in water. The analytical values of the products of reaction in the final stage agree with the equation

$$2KIO_4 + 5H_2S = K_2SO_4 + 2HI + 4H_2O + 4S \quad \ldots \quad \ldots (3)$$

In course of the reaction during experiments No. 4 and 5, the IO_3' and I' contents perhaps further undergo a reaction shown by the equation

$$KIO_3 + KI + H_2O + 2S = K_2SO_4 + H_2S + I_2 \quad \ldots \quad \ldots (4)$$

and the iodine, thus liberated, leads to the formation of HI as shown by equation (2). This seems to be in agreement with the experimental observations. The analytical data further indicate that the reaction (2) starts only when whole of IO_3' has been consumed and therefore in all those stages when IO_3' is present H_2S has no tendency to react with free iodine to produce any HI.

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INTERFACIAL TENSION AND COMPLEX FORMATION. THE SYSTEM $BaCl_2$—ALKALI CHLORIDE—H_2O

By H. V. Barot and C. M. Desai

With increasing dilution of the mixed salt solutions of barium chloride and potassium or ammonium or sodium chloride in water, the number of complexes formed between barium and alkali chlorides has been found to vary from three to six or seven. When six out of seven complexes are observed, one of them obtained with sodium chloride is not evident with potassium, ammonium or lithium chloride. With lithium chloride only three to six complexes appear with decrease in salt concentrations.

Desai and Kazi (this *Journal*, 1953, **30**, 421, 426) have shown the variation in the nature and number of molecular complexes in mercuric chloride-alkali chloride-water system with change in salt concentrations. Such variations have been also observed with other systems (Desai and Kazi, *Science & Culture*, 1953, **19**, 259). The present work forms a part of an extended investigation of the nature and number of complexes, observed with barium, strontium, calcium or magnesium chloride-alkali chloride-water systems. In this paper the results obtained with barium chloride system are reported.

Barium chloride forms double salts with potassium chloride in solid state or in aqueous solution. Some of them, reported to exist in solid state, are $2KCl.BaCl_2$; $3KCl.BaCl_2$; $KCl.3BaCl_2$ (Vortisch, *Jahrb. Min. Beil. Bo.*, 1914, **38**, 186 ; Gemsky, *J. Chem. Soc.*, 1914, **106**, 51 ; Elchardus and Laffitte, *Bull. soc. chim.*, 1932, **51**, 1572; Sato, *Kinz. No. Kenk*, 1933, **10**, 448). The existence for $2KCl.BaCl_2$ and $KCl.2BaCl_2$ in solution was shown by refractometric results (Spacu and Poper, *Z. physikal. Chem.*, 1899, **B30**, 113).

Srivastav and Bose (this *Journal*, 1953, **30**, 411) have shown the formation of seven complexes: $4KCl.BaCl_2$, $3KCl.BaCl_2$, $2KCl.BaCl_2$, $3KCl.2BaCl_2$, $KCl.BaCl_2$, $2KCl.3BaCl_2$ and $KCl.2BaCl_2$ in the mixed solutions of these salts by means of viscosity data.

Experimental

The salts used were of standard quality and recrystallised. Series of mixed solutions of barium chloride and alkali chloride each, were prepared by the method described by Desai (this *Journal*, 1954, **31**, 957) for interfacial tension measurements against *n*-butyl acetate. The composition of the complexes are shown in the last column of the table in which a = 4B. A, b = 3B. A, c = 2B. A, d = 3B.2A, e = B. A, f = 2B. 3A, g = B.2A,

Conc.	Salt A.	Salt B.	Peaks correspond to
M/1	$BaCl_2$	KCl or NH_4Cl	c, e, g
M/2	,,	,,	a, c, d, e, f, g.
M/40	,,	,,	a, b, c, d, e, f, g
M/1	,,	NaCl	c, e, g
M/2	,,	,,	b, c, d, e, f, g
M/40	,,	,,	a, b, c, d, e, f, g
M/500	,,	LiCl	a, c, d, e, f, g
M/20	,,	,,	c,

For the series ($M/40$) potassium, ammonium and sodium chloride seven peaks (a, b, c, d, e, f, g) are observed, while for the series ($M/2$) potassium, ammonium and sodium chloride and ($M/500$) lithium chloride, only six complexes are evident with the result that the complex (b) disappears in the potassium, ammonium and lithium systems, and the complex (a) disappears in the sodium system. With the series ($M/1$) potassium, ammonium or sodium chloride and ($M/200$) lithium chloride, only three complexes (c), (e) and (g) are evident.

Thus, the number of complexes in the mixed solutions of the barium and alkali chlorides varies as three, six or seven as the composition of the mixed solution changes with respect to decreasing salt concentrations.

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INTERFACIAL TENSION AND COMPLEX FORMATION OF METAL SULPHATES

By Hemlata Kazi

Sulphates of copper, cabalt, nickel, vanadium, zinc, magnesium and cadmium form with alkali sulphates two complexes in mixed solution, while silver sulphate and alkali sulphates form only one complex in their mixed solutions, and bivalent metal sulphates form three complexes in the mixed solution of any two such sulphates.

Complex anions, $Cu(SO_4)_2^{2-}$, in the solution of double sulphate $K_2Cu(SO_4)_2$ were detected by Rieger (*Z. Elektrochem.*, 1901, **7**, 863, 871). Pfanhauser (*ibid.*, 1901, **7**, 698) found the complex anion $Ni(SO_4)_2^{2-}$ in the solution of nickel ammonium sulphate. McBain and Rysselberge (*J. Amer. Chem. Soc.*, 1928, **50**, 3009; 1930, **52**, 2336) indicated the presence of complex anions $M(SO_4)_2^{2-}$ formed by adding a large excess of sulphate ions (alkali sulphate) to a divalent sulphate (Mg, Zn, Cd) by means of transference measurements. They have further shown that these complex anions cannot be considered as negligible in dilute solutions also. These are probably formed by the combination of ordinary undissociated molecules with ions.

The complex formation in solution between different metal nitrates and chlorides with alkali nitrates and chlorides respectively was reported in the previous work (Desai and Kazi, this *Journal*, 1953, **30**, 290, 427; *Science & Culture*, 1953, **19**, 259; Hemlata Kazi, this *Journal*, 1954, **31**, 763). Such possibility between various metal sulphates by means of interfacial tension measurements against *n*-butyl or *iso*amyl acetate has been investigated.

Experimental

The salts used were of standard quality. Series of mixed solutions were prepared by the monovariation method (*loc.cit.*). The tension values of the mixed solutions with the ester were plotted against the volume of the variant A. The compositions of the complexes, indicated by the peaks in the graphs, are shown in the last column of the table in which a = A. 2 B, b = A.B and c = 2A.B.

The results indicate that the sulphates of copper, nickel, cobalt, vanadium, magnesium, zinc and cadmium form two complexes (a) and (b) with potassium, sodium, lithium and ammonium sulphates. Silver and alkali sulphates form only one complex (b) in the mixed solutions of any two of these sulphates, while copper, nickel, cobalt, vanadium, magnesium, zinc or cadmium sulphate forms three complexes (a, b, c) in the mixed solutions of any two of these sulphates.

TABLE I

Conc.	Salt A.	Salt B.	Peaks correspond to	Conc. (M	Salt A.	Salt B.	Peaks correspond to
M/50	$ZnSO_4$	$(NH_4)_2SO_4$	a,b	*M*/1000	VSO_4	Na_2SO_4 or $(NH_4)_2SO_4$	a,b
M/500	,,	,,	a,b	*M*/100	$(NH_4)_2SO_4$	Ag_2SO_4	b
M/10	,,	Na_2SO_4	a,b	*M*/100	Li_2SO_4	,,	b
M/50	,,	K_2SO_4 or Li_2SO_4	a,b	*M*/100	Na_2SO_4	,,	b
M/1.1	$CuSO_4$	Na_2SO_4	a,b	*M*/1.0	$(NH_4)_2SO_4$	Na_2SO_4	b
M/50	,,	K_2SO_4 or $(NH_4)_2SO_4$ or Li_2SO_4	a,b	*M*/2	Na_2SO_4	Li_2SO_4	b
				M/100	K_2SO_4	Na_2SO_4	b
M/20	$MgSO_4$	Li_2SO_4	a,b	*M*/100	VSO_4	$CoSO_4$	a,b,c
M/1	,,	,,	a,b	*M*/100	$MgSO_4$	VSO_4	a,b,c
M/1000	,,	,,	a,b	*M*/100	$CuSO_4$	$ZnSO_4$	a,b,c
M/50	,,	K_2SO_4 or Na_2SO_4 or $(NH_4)_2SO_4$	a,b	*M*/100	$CdSO_4$	$NiSO_4$	a,b,c
M/60	$CoSO_4$	$(NH_4)_2SO_4$ or K_2SO_4	a,b	*M*/100	$CdSO_4$	$MgSO_4$	a,b,c
M/50	,,	Li_2SO_4	a,b	*M*/100	$ZnSO_4$	$NiSO_4$	a,b,c
M/10	$NiSO_4$	Na_2SO_4 or Li_2SO_4	a,b	*M*/100	$CoSO_4$	$CuSO_4$	a,b,c
M/20	VSO_4	Li_2SO_4 or K_2SO_4	a,b				

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ACTION OF SULPHUROUS ACID ON ALKALINE POTASSIUM PERMANGANATE

By Kundan Lal and Gurdev Singh

When normal sulphurous acid reacts with potassium permanganate solution (50 c.c., 1%), treated with varying amounts of potassium hydroxide till the pink colour is just discharged, a precipitate of the general composition, $x\ K_2O.\ y\ MnO.\ z\ MnO_2$, is formed. In the acidic medium the reaction leads to the formation of sulphates of potassium and manganese along with some potassium dithionate, but in the alkaline medium potassium sulphate is the only product of reaction and the entire amount of manganese remains in the precipitate.

In the previous communication it has been shown that the action of potassium sulphite on potassium permanganate leads to the formation of compounds of various composition, *i.e.*, $xK_2O.\ yMnO.\ zMnO_2$, alkali sulphite being completely oxidised to sulphate (this *Journal*, 1954, **31**, 410). The present work records the action of sulphurous acid on alkaline permanganate solution.

Experimental

Sulphurous acid was prepared by bubbling sulphur dioxide gas, obtained by heating potassium bisulphite with dilute sulphuric acid, through a bottle filled with distilled water and surrounded by ice water. It was made exactly normal by dilution and then added dropwise with constant shaking to $KMnO_4$ solution (50 c.c., 1%), treated with 4 c.c. of *N*-KOH solution, taken in each of the two beakers, surrounded by ice water, until the pink colour was just discharged. The dark brown precipitate, thus formed, was filtered, washed and analysed. It was found to contain manganese dioxide, manganese oxide and potassium oxide, which were estimated by the methods described by Mohammed and Bedi (this *Journal*, 1944, **21**, 55). A compound of the composition $K_2O.\ 3MnO.\ 24MnO_2$ was observed to be formed. The filtrate from the precipitate was found to contain free sulphuric acid and sulphates of potassium and manganese. Formation of a small amount of potassium dithionate was also detected since the solution, after the removal of sulphate as barium sulphate in cold, on treatment with strong hydrochloric acid gave small quantities of sulphur dioxide and sulphate (Mohammed and Ahluwalia, *ibid.*, 1941, **18**, 309). Thiosulphate and sulphite were found to be absent among the products of reaction. Sulphuric acid was estimated by titrating it against a standard KOH solution using Bromocresol green (0.1% alcoholic solution) as an indicator. Sulphate was determined as barium sulphate in cold (Mitchel, "Modern Methods of Chemical Analysis", p.136). Potassium was estimated by sodium cobaltinitrite method. A known portion of the filtrate was treated with potassium bromate and strong hydrochloric acid to oxidise any potassium dithionate. The total sulphate was precipitated as barium sulphate in cold (*loc.cit.*). The amount of manganese in the filtrate, being very small, was determined by subtracting the amount of manganese observed in the precipitate from the total added.

Again, the experiments were performed in duplicate with 6,8,10, and 12 c.c. of KOH solution, exactly in the similar way. The analytical results of the various products of reaction are recorded in Table I.

TABLE I

Normal solutions of H_2SO_3 and KOH used. $KMnO_4$ = 50 c.c. (1%).

KOH added.	H_2SO_3 added.	K_2SO_4 formed	$K_2S_2O_6$ formed.	H_2SO_4 formed.	KOH (obs.)	$MnSO_4$ formed.	K_2O : MnO : MnO_2. Mol. ratio (approx.)	MnO : MnO_2. Mol. ratio (approx.)
4.0 c.c.	11.82 c.c.	0.5843 g.	0.0268 g.	0.1463 g.	Nil	0.0265 g.	1 : 3 : 24	1 : 8
	11.68	0.5810	0.0290	0.1447		0.0261	1 : 3 : 24	1 : 8
6.0	11.80	0.7592	0.0222	0.0518		0.0179	1 : 2 : 16	1 : 8
	11.85	0.7629	0.0194	0.0503	,,	0.0203	1 : 2 : 16	1 : 8
8.0	11.95	0.8650	0.0116			0.0135	2 : 1 : 7	1 : 7
	11.85	0.8667	0.0122	Nil		0.0129	2 : 1 : 7	1 : 7
10.0	11.88	0.8979			0.0785 g.		1 : 1 : 4	1 : 4
	12.02	0.8965	Nil	,,	0.0796	,,	1 : 1 : 4	1 : 4
12.0	11.95	0.8977	,,	,,	0.1833	,,	1 : 1 : 4	1 : 4
	11.95	0.8953			0.1840		1 : 1 : 4	1 : 4

Due to the formation of sulphuric acid, the filtrate in the beginning was acidic. It became neutral and ultimately alkaline in the further experiments. Manganese in the alkaline filtrate was found to be absent.

Manganese dioxide, which is the first product of reaction, probably reacts with sulphurous acid in the acidic medium forming dithionate according to the equation,

$$MnO_2 + 2\,H_2SO_3 = MnS_2O_6 + 2\,H_2O \quad \ldots \quad (1)$$

and manganese dithionate further reacts with potassium oxide as shown by the equation,

$$MnS_2O_6 + K_2O = K_2S_2O_6 + MnO \quad \ldots \quad (2)$$

The reaction represented by equation (1) does not take place in the alkaline medium, and therefore no dithionate is observed in the alkaline filtrate. Manganese sulphate is one of the products of reaction in the acidic medium. It becomes minimum in the neutral filtrate and vanishes when the filtrate becomes alkaline. Formation of manganese sulphate may be due to the interaction of such manganese oxide as formed by equation (2) and the sulphuric acid formed during the reaction. Further, since formation of manganese dithionate decreases with the increasing volumes of potassium hydroxide solution, the resulting manganese oxide and ultimately manganese sulphate too suffer a corresponding decrease. Potassium sulphate content increases to a maximum till the filtrate becomes alkaline and then it remains constant. This may be due to the neutralisation of sulphuric acid by the excessive additions of potassium hydroxide.

Manganese dioxide content remains constant up to the neutral stage. It further decreases and remains unchanged afterwards. Manganese oxide content increases slowly up to the neutral stage, and suddenly as the medium becomes alkaline and then

remains constant. This may partly be due to the reduction of some of manganese dioxide to manganese oxide by sulphurous acid and partly due to decomposition of manganese sulphate by alkali.

In the acidic medium the molecular ratio of K_2O : MnO : MnO_2 is 1 : 3 : 24 in the first and 1 : 2 : 16 in the second experiment. It becomes 2 : 1 : 7 in the neutral and 1 : 1 : 4 throughout the alkaline medium. The ratio of MnO : MnO_2 has further been observed to be 1 : 8 during the acidic and 1 : 4 throughout the alkaline stage of the reaction. The compound formed in the alkaline stage of this reaction agrees with that already obtained by the action of normal potassium sulphite solution on 1% potassium permanganate solution (Lal and Singh, *loc. cit.*). According to Cocosinschy (*Z. anorg. Chem.*, 1930, **176**, 186; 1930, **293**, 189) the formation of these polypermanganites, resulting on account of the feebly acidic properties of hydrated manganese dioxide, may be due to a polypermanganous acid $H_2Mn_2O_5$, which is thought to be formed in the preliminary stage of the reaction.

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NATIONAL CHEMICAL LABORATORY OF INDIA
POONA

CSIR Scheme on "Preparation of Research Chemicals for India"

Arrangements for the preparation and supply of the following chemicals at reasonable rates have been made :

Acetylphenylhydrazine
2-Acetylresorcin
Acid phenyl-arsonic
Aconitic acid
l-Alanine
Aluminium chloride (anhydrous)
p-Amino-acetophenone

β-Aminoanthraquinone
Anthraquinone
Anthraquinone-2-sodium sulphonate
l-Arginine monohydrochloride

Benzanthrone
Benzeneazo-*β*-naphthol
Benzenesulphonic acid (sodium salt)
Benzhydrazide
Benzidine
Benzylic acid
Benzoic anhydride
Benzoylacetone
p-Bromophenacyl bromide
N-Bromosuccinimide
p-Bromophenylhydrazine hydrochloride
Butanone-2
carbazole
Casein hydrolysate (vitamin-free)
β-Chloroanthraquinone
Chlorobenzene
p-Chloromercuri-benzoic acid
4-Chloro-2-methylphenoxyacetic acid
Congo red
l-Crystine

2 :5-Dichloronitrobenzene
2 :6-Dichlorophenol-indophenol
2 :2′-Dihydroxy-1 :1′-dinaphthyl

p-Dimethylaminobenzaldehyde
β-Dimethylaminomethyl-indole
m-Dinitrobeznene
2 :4-Dinitro-*α*-naphthol
2 :4-Dinitrochlorobenzene
Diphenylcarbazide
as-Diphenylhydrazine hydrochloride
Diphenyl ketone
Diphenylthiocarbazone

Egg albumin (non-cryst.)
Ethyl acetone-dicarboxylate

l-Glutamic acid
Glycerol monochlorohydrin

Heptanone-4
l-Histidine monohydrochloride
8-Hydroxyquinaldine
8-Hydroxyquinoline

Indole-3-acetic acid
Isatin
Itaconic acid

l-Leucine
Levulinic acid
Linoleic acid

Maleic hydrazide
α-Methyl-*α*-phenylhydrazine sulphate

Naphthalene-*β*-sulphonic acid (sodium salt)
1 :2-Naphthaquinone-4-sulphonic acid (Na & K salts)
Ninhydrin
m-Nitroaniline

o-Nitrobenzaldehyde
p-Nitrobenzeneazo-*α*-naphthol
α-Nitronaphthalene
m-Nitrophenol
o-Nitrophenol
1-Nitroso-2-naphthol

Oleic acid

Palmitic acid
Pentanone-3
N-Phenylanthranilic acid
Phenylhydrazine hydrochloride
Phosphomolybdic acid
Phosphotungstic acid
Potassium hydrogen phtnalate
α-Pyridylmethyl ketoxime
Pyruvic acid

Salicyl aldehyde
Skatole
Sodium iodo-acetate
Stearic acid
Stilbenediamine hydrochloride
Succinimide
Sulphanilic acid

αβγδ-Tetraphenylporphine
Titanium trichloride solution
αβγ Triaminopropane hydrochloride
p-Tolyl mercuric chloride
Trichloroacetic acid
Tryptophane
l-Tyrosine

Urease (water melon)

Preparations of some other chemicals can also be arrranged. Enquiries from Heads of Research Institutes are welcome. Please write to the Director, N. C. L., Poona 8.

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[Jour. Indian Chem. Soc., Vol. 32, No. 2, 1955]

DERIVATION OF A NEW EXPRESSION CONNECTING SURFACE CONDUCTIVITY WITH THE TRUE AND APPARENT ZETA-POTENTIALS OF PARTICLES FORMING A DIAPHRAGM

By B. N. Ghosh

For a diaphragm consisting of spherical particles of radius, r, the following expression, connecting the specific surface conductivity, $p\lambda$, with the true and apparent zeta potentials, ζ and ζ_a respectively, has been deduced

$$\xi/\xi_a = 1 + \frac{3p\lambda}{a\,r\,S} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

where a represents the ratio of the volume of the liquid phase to the volume of the solid phase in the diaphragm and S, the specific conductivity of the liquid in bulk. It has been shown that equation (1) may be expressed as

$$\xi/\xi_a = 1 + \frac{\alpha}{S}\,(K_p - S)$$

where K_p represents the specific conductivity of the liquid inside the pores of the diaphragm. It has also been shown that the other equations such as

$$\xi/\xi_a = 1 + \frac{m}{r} \quad \text{and} \quad \xi/\xi_a = 1 + \frac{m}{S}$$

used by the author and co-workers in previous publications, can be deduced from equation (1).

It has been reported in a number of papers by Ghosh, and Ghosh and co-workers (this *Journal*, 1954, **31**, 273, 393) that the true zeta-potential of particles forming a diaphragm can be found from the equation

$$\frac{\xi}{\xi_a} = 1 + \frac{\alpha}{S}(K_p - S)$$

where ξ and ξ_a represent the true and apparent zeta potentials respectively, K_p, the specific conductivity of the liquid inside the pores of the diaphragm and, S, its bulk specific conductivity. The factor α is a constant and has been found to depend on the state of compression of the diaphragm.

An attempt has been made in this paper to derive a relatively complete expression taking the structure and the state of compression of the diaphragm into consideration.

Let us assume that the diaphragm is a porous structure and at a given tightness of packing, the average radius and length of a representative pore be d and l cm. respectively. Hence, the volume of this pore is $\pi d^2 l$. Let r be the radius of each particle and $a \times \frac{4}{3}\pi r^3$ be the 'free space', v, associated with each particle in the diaphragm, so that

$$\frac{1}{a} = \frac{4\pi r^3}{3v}.$$

Hence, the total number of particles which will be associated with the free space, $\pi d^2 l$, of the pore is $\pi d^2 l / \frac{4}{3}\pi r^3 a$ and these particles will form the walls of the pore. The surface area of each of these particles is $4\pi r^2$ and if p be the number of electrically charged points per unit area of the surface, then the total number of such charged points each carrying, say unit charge per pore is

$$\frac{\pi d^2 l}{\frac{4}{3}\pi r^3 a} \times 4\pi r^2 p \quad \text{or} \quad \frac{3\pi d^2 l p}{ra}.$$

Let us further assume that the contribution of each charged point towards electrolytic conductance be λ, which may vary with ξ and, therefore, with the concentration, or S of a given electrolyte solution filling the pores of the diaphragm. Hence, for a given value of a, the specific conductivity of the liquid inside the pore, should be given by the expression,

$$\left\{\frac{3\pi d^2 l p\lambda}{ra}+S(\pi d^2 l)\right\}\frac{1}{\pi d^2 l}$$

$$\text{or } S\left(1+\frac{3p\lambda}{raS}\right).$$

The electro-osmotic behaviour of this pore of radius d, length l, and specific surface conductivity $p\lambda$ is therefore given by the equation

$$\xi/\xi_a = 1+\frac{3p\lambda}{raS} \quad \ldots \quad \ldots \quad (1)$$

It is evident from equation (1) that ξ_a will decrease as a decreases, *i.e.* as the state of compression of the diaphragm increases. This has been found to be the case for the filter papers (S and S) and has been reported by Ghosh and Ghosh in a previous paper (this *Journal*, 1954, **31**, 649).

It also follows from equation (1) that $1/\xi_a$ plotted against $1/r$ will give a straight line when all the other factors are constant. It has been shown by Ghosh, Rakshit and Chattoraj (*ibid.*, 1953, **30**, 601) that this conclusion is confirmed by Bull and Gortner's data on quartz particles. Again when r, a, p, and ξ remain constant and S varies, it follows from equation (1) that the relation between $1/\xi_a$ and $1/S$ should be linear. This has been confirmed in the cases of titanium oxide and silver iodide sols in the presence of equicoagulating concentration of electrolytes (*Trans. Faraday Soc.*, 1954, **50**, 729).

If we now replace the pore by a smooth capillary tube having exactly the same radius d, length l, and specific surface conductivity $p\lambda$, and filled with the same solution, then its electro-osmotic behaviour will be represented by the equation (Rutgers, *Trans. Faraday Soc.*, 1940, **35**, 69),

$$\xi/\xi_a = 1+\frac{2p\lambda}{dS} = 1+\frac{(K_p-S)}{S} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where $(K_p—S)$ stands for $2p\lambda/d$, and K_p represents the specific conductivity of the liquid inside the capillary tube.

Substituting the same value of $2p\lambda/d$ in equation (1), we get the equation of the pore in the following form :

$$\xi/\xi_a = 1+\frac{3}{2}\times\frac{d}{ra}\times\frac{(K_p-S)}{S} \quad \ldots \quad \ldots \quad (3)$$

Thus the difference between the electro-osmotic equation of the pore and that of the equivalent capillary tube lies in the factor $\frac{3}{2}\times\frac{d}{ra}$, with which $\frac{K_p-S}{S}$ is multiplied. Hence to obtain

the electro-osmotic equation of a diaphragm, $(K_p - S)/S$, in the corresponding equation of the equivalent capillary tube, will have to be multiplied by the factor, $\frac{3}{2} \times \frac{d}{ra}$, where d, r and a have the same significance as stated already. Therefore, for a diaphragm, we can use the equation

$$\xi/\xi_a = 1 + \frac{\alpha}{S}(K_p - S) \qquad (4)$$

where α stands for $\frac{3}{2} \times \frac{d}{ra}$. It may also be pointed out that for given values of r and a, d has got a definite value and that since a represents the ratio of the volume of the liquid to that of the solid phase in the diaphragm, at very high compression, $1/a$ should approach the limiting value 3.2.

In the foregoing deductions it has been assumed that the diaphragm is formed by uniform spherical particles, each of radius r. If uniform cylindrical particles, of radius r, and length l, be used instead, then 3, in equations (1) and (3) is to be replaced by 2. This can be easily proved by following the same line of argument as has been used above, neglecting the surface area of the two ends.

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HYDROLYSIS OF ETHYL ACETATE IN HYDROCHLORIC ACID SOLUTIONS CONTAINING GLUCOSE

By Hussein Sadek and M. S. Abu Elamayem

Hydrolysis of ethyl acetate in 0.05*N*-HCl at 30°, 35°, 40° and 45° was carried out in the absence and presence of glucose. The addition of glucose lowers the velocity constant while the activation energy remains constant. The results are in favour of intermolecular attraction between glucose and hydrogen ions.

The work of Hinshelwood and his co-workers (*J. Chem. Soc.*, 1938, 848 ; 1936, 1937) has already shown that in the case of ethyl acetate, the activation energy is independent of the temperature in the range of 25°—80°, where aqueous mixtures with ethyl alcohol or acetone are used as solvent. Also, Harned and Ross (*J. Amer. Chem. Soc.*, 1941, **63,** 1993) showed that the activation energy of the acid hydrolysis of methyl acetate in dioxane-water mixtures was independent of the solvent composition. However, the activation energy of the hydrolysis of methyl acetate in aqueous solution was found to decrease with rise in temperature (McKinley, McKee and Moelwyn Hughes, *Trans. Faraday Soc.*, 1952, **48,** 247). The present work was carried out in order to detect any variation of the activation energy of the acid hydrolysis of ethyl acetate in the presence of glucose which in aqueous solution gave a dielectric constant close to that of water, in contrast to the organic solvent component used by the previous authors. It has been shown (Sadek and Zayan, this *Journal*, 1953, **30,** 823) that the addition of glucose to dilute aqueous hydrochloric acid solutions lowers the p_H value. Since the hydrolysis of esters depends on the hydrogen-ion concentration, the question which arises is : to what extent does the addition of glucose influence the velocity of the hydrolysis reaction ?

Experimental

Ethyl acetate of "Merck" quality was distilled in an all-pyrex glass apparatus with a fractionating column 60 cm. long. The middle fraction (b.p. 76°—76.9°) was collected. All hydrolysis experiments were carried out using a fixed initial quantity of the ester (0.0203 mole) and 0.0500 *N*-HCl solution. The rate of the reaction was measured at 30°, 35°, 40° and 45°. The reaction vessel was a 100 ml. pyrex flask provided with a small bulb in its neck, which served to collect any condensed vapours. Hydrolysis in glucose-hydrochloric acid solution was carried out using 4 and 8 weight percent glucose in a thermostat accurate to $\pm 0.02°$.

Rate of Hydrolysis.—The results in pure acid solutions were always compared with those containing glucose. The rate of the reaction was followed by withdrawing 2 ml. sample (using a calibrated graduated micropipette accutate to 0.01 ml.) for analysis after several time intervals. The samples were chilled, diluted with conductivity water and titrated against standard alkali using phenolpthalein as an indicator in CO_2-free atmosphere. The initial concentration of the ester was determined by analysing several samples which were hydrolysed in sealed tubes for 2 days at 100° and then titrated against 0.0448*N*-NaOH. The infinity values thus obtained agreed within 0.3%. Correction was made for the amount of alkali required to neutralise the acid obtained from the hydrolysis in pure water.

TABLE I

t.	x_0.	$a-x_0$.	x_4.	$a-x_4$.	x_8.	$a-x_8$.
660 min.	6.52	26.07	4.79	27.80	4.08	28.51
930	9.36	23.23	7.53	25.06	6.71	25.88
1080	10.80	21.79	8.93	23.66	8.16	24.43
1200	11.70	20.89	10.01	22.58	9.12	23.47
1320	12.87	19.72	11.07	21.52	10.15	22.44
1440	13.89	18.70	12.09	20.50	11.23	21.37
1530	14.65	17.94	12.79	19.80	11.93	20.66
1680	15.67	16.92	13.91	18.68	13.07	19.52
1800	16.52	16.07	14.81	17.78	13.78	18.81
1920	17.29	15.30	15.47	17.12	14.40	18.18
2160	18.85	13.74	17.21	15.38	16.11	16.48
2760	21.92	10.67	20.40	12.19	19.40	13.19
	32.59	0.00	32.59	0.00	32.59	0.00

TABLE II

Temp.	$10^4 \times k_0$.	$10^4 \times k_4$.	$10^4 \times k_8$.
30°	4.275 min^{-1}	3.914 min^{-1}	3.690 min^{-1}
35°	6.365	5.842	5.434
40°	9.863	9.230	8.226
45°	14.19	13.05	12.18

DISCUSSION

Table I records the results of typical experiments at 30° in the absence and in presence of glucose. The velocity constant was calculated from a plot of $\log (a-x)$ against t, where a is the initial concentration of ethyl acetate and x is the hydrogen-ion concentration at the time t in minutes. The subscripts refer to the percentage of glucose in solution. In Table II the values of the velocity constants at different temperatures are recorded. The activation energies calculated from these data are constant and equal to: E_0=15.55, E_4=15.37 and F_8=15.35 k.cal./mole.

It is quite remarkable to find that the addition of glucose lowers the velocity constant below that in pure acid solution while the activation energy remains almost constant. However, the lowering of the p_H value of hydrochloric acid solutions by the addition of glucose was partly explained as being due to hydration of glucose in solution. The hydration of glucose would thus be expected to act in an opposite manner tending to increase the acid concentration, and hence, increasing the rate of hydrolysis. A lowering of the velocity constant should require an increase in the activation energy if the entropy factor remains constant. The above results indicate a decrease in the entropy factor on the addition of glucose, as can be seen from Table III.

TABLE III

Glucose	0%.	4%.	8%.
At 30°			
ΔF	24.90 k.cal./mole	24.96 k.cal./mole	24.93 k.cal./mole
ΔH	14.79	14.77	14.75
$-\Delta S$	0.0315 k.cal./deg./mole	0.0336 k. cal./deg./mole	0.0338 k.cal./deg./mole
At 35°			
ΔF	26.29	26.35	26.39
ΔH	14.78	14.76	14.74
$-\Delta S$	0.0365	0.0376	0.0378
At 40°			
ΔF	25.22	25.25	25.33
ΔH	14.77	14.75	14.73
$-\Delta S$	0.0329	0.0336	0.0339
At 45°			
ΔF	25.39	25.44	25.48
ΔH	14.76	14.74	14.72
$-\Delta S$	0.0329	0.0337	0.0339

The decrease in the reaction rate by the addition of glucose may be due to a reaction between glucose and hydrogen ions according to the scheme :

$$\text{Glucose} + H_3O^+ \rightleftarrows (\text{glucose}, H_3O)^+$$

(Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **60,** 2891 ; Amis and Holmes *ibid.* 1941, **63,** 2231). The resulting glucose-proton complex would thus have no catalytic activity, and the decrease in the reaction rate is thus easily explained. This finding supports the view that electrostatic interaction occurs between hydrogen ions and glucose (Sadek and Zayan, *loc. cit.*).

Furthermore, it can be seen from Table III that the entropy change is quite marked in 4% glucose solution; with the further addition of glucose the entropy change suffers a small change. This result suggests that as glucose is added to hydrochloric acid, a definite proportion of the hydrogen ions is involved in electrostatic combination with glucose. The calculations shown in Table IV confirm this view.

The catalytic coefficient k is given by the expression,

$$k_2 = k_{obs.} / [H^+]$$

The value of k_2 is obtained by substituting for $k_{obs.}$ the values in pure acid solution at the given temperature. The catalytically active hydrogen-ion concentration in the solutions containing glucose is thus readily calculated. The difference between the concentrations obtained and the original concentration of HCl (0.0500 *N*) gives the concentration of hydrogen ions involved in combination with glucose. Values of $[H^+_{comb.}]$ per mole of glucose are shown in Table IV.

TABLE IV

% Glucose.	Temperatures 30°.	35°.	40°.	45°.	Mean.
4	0.0177	0.0180	0.0146	0.0181	0.0171
8	0.0153	0.0164	0.0188	0.0161	0.0166

It can be seen that the above values are nearly independent of temperature and glucose concentration.

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A STUDY OF INFRA-RED SPECTRA OF ACONITINE, DELPHININE AND THEIR ALKAMINES

By Bhola Nath

The infra-red spectra of aconitine, delphinine, aconine and delphonine have been examined. The bands reveal a marked similarity in the functional groups as well as nuclear features. One hydroxyl group is detected to be involved in H-bonding, and the possible existence of a non-conjugated double bond (C=C) is indicated.

Beyond the functional groups not much work is reported in literature (Henry, "Plant Alkaloids", 1949, pp. 674, 697) on the chemistry of aconitine and delphinine alkaloids due probably to some unusual nuclear features. As infra-red bands are diagnostic in many respects, aconitine, delphinine, aconine and delphonine have been spectroscopically examined and their spectra recorded. Some useful information, not available from other sources, is embodied in this communication.

The infra-red spectra have been recorded with a Grubb Parson's single beam instrument (NaCl ; powder spectra).

Lithium aluminium hydride reduces aconitine and delphinine to aconine and delphonine respectively and all the attempts to bring about further reduction of the alkamines by using even excess reagent and for a prolonged period were unsuccessful.

Delphinine.—A band at about 3.03 μ indicates the presence of one OH group involved in H-bonding. A band at 5.95 μ indicates the presence of a carbonyl group and/or a non-conjugated C=C group. A strong band at 9.17 μ suggests the presence of an ether linkage (aliphatic).

Aconitine.—A band near 3.03 μ indicates the presence of -OH group involved in H-bonding. The band near 5.89 μ is due to the carbonyl and/or a non-conjugated C=C group, and the strong absorption near 9.10 μ is produced (at least in part) by the aliphatic ether linkage. Besides these bands similar to delphinine, aconitine spectrum contains several additional strong bands, e.g. near 9.62, 8.77 and 7.69 μ which could be due to structural groupings not present in delphinine, possibly arising from O—H links.

Delphonine.—A band at about 3.03 μ indicates the presence of an -OH group involved in H-bonding. A band at 6.04 μ indicates the presence of a non-conjugated C=C. A strong band at about 9.17 μ suggests the presence of an ether linkage of aliphatic type.

Aconine.—A band at 3.03 μ indicates the presence of an -OH group involved in H-bonding. A band at 6.02 μ indicates the presence of a non-conjugated C=C group. An intense band at 9.12 μ suggests the presence of an ether linkage.

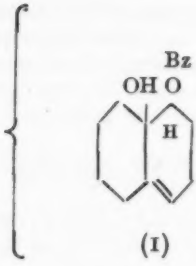
Experimental

$LiAlH_4$ *Reduction of Delphinine.*—A solution of delphinine (50 mg.) in dry ether (10 ml.) was added to a stirred solution of lithium aluminium hydride (excess) in ether, the mixture refluxed for 20 hours and the complex broken with 10% sulphuric acid. The clear solution was made alkaline with potassium carbonate, extracted with ether, the extract washed with water, dried (Na_2SO_4) and the solvent removed, yielding a glassy resin, m.p. 76-77°, not depressed by admixture with authentic delphonine. (Found : C, 63.5 ; H, 8.69. $C_{24}H_{39}O_7N$ requires C, 63.6 ; H, 8.6 per cent).

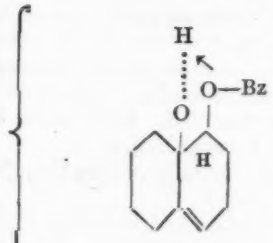
$LiAlH_4$ *Reduction of Aconitine.*—A solution of aconitine (10 mg.) in benzene (10 ml.) was added to lithium aluminium hydride (excess) in ether (10 ml.) and the mixture refluxed for 6 hours and worked up as above, yielding an amorphous powder, m.p. and mixed m.p. with authentic aconine, 129-31°.

Discussion

(*a*) H-*Bonding.*—Delphinine contains one -OH group. Jacobs and Sato (*J. Biol. Chem.*, 1949, **180**, 133, 479) tentatively suggested that this group existed as a tertiary hydroxyl adjacent to a secondary hydroxyl group which was protected by a benzoyl group as (I).



(I)



(II)

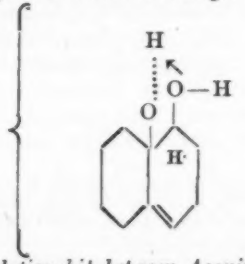
Beyond this the chemical means and the ultraviolet absorption spectrum have failed to throw any light. Hence, OH group has been regarded as a simple hydroxyl group.

Infra-red spectroscopy offers a very promising approach to this aspect. Absorption in the region 9.10 to 7.69 μ, characteristic of the ordinary type of -OH group, is entirely absent in the spectrum, whereas a band at 3.03 μ indicates the presence of the -OH group involved in H-bonding. This hydroxyl group is so favourably placed as to receive electrons from a donor oxygen within the molecule and consequently intramolecular bonds O.....H.....O are set up as part of a chelate ring system.

Aconitine contains three free hydroxyl groups. Chemical reactions and ultraviolet absorption spectrum do not show any distinctive features between them. But the infra-red spectral study clearly demonstrates that at least one of the three OH groups is chelated in hydrogen bonding and gives rise to a band at 3.03 μ. On the contrary, the other two -OH groups, which are possibly alike in themselves but entirely different from this chelated one, produce strong bands in the region 9.62 to 7.69 μ. The five-membered chelated ring (Sidgwick, 'The Electronic Theory of Valency', 1927, pp. 238, 243, 245; Remick, "Electronic Interpretation of Org. Chem." 1946, p. 43 ; Lassettre, *Chem. Rev.*, 1937, **20,** 272, 301 ; Auwers, *Z. physikal. Chem.*, 1900, **32,** 39 ; Sidgwick and Callow, *J. Chem. Soc.*, 1924, **125,** 533; Coulson, "Valence", Oxford, Clarendon Press, 1952, p. 299) may be represented as (II) in delphinine and aconitine.

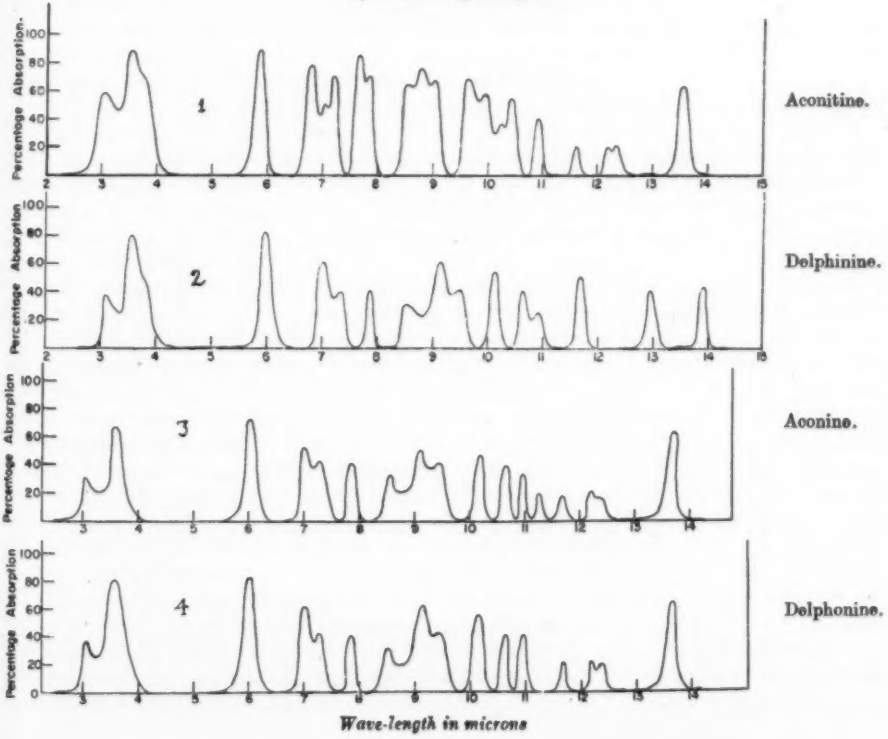
The infra-red spectrum of delphonine (also aconine) still contains a band at 3.03μ and shows that the elimination of the benzoyl group by alkaline hydrolysis does not disturb the chelation. Apparently the tertiary -OH group retains the property of electron acceptor and the oxygen atom that acted as electron-donor before hydrolysis keeps on doing so even after hydrolysis. The five-membered chelate ring system remains intact as (III) or takes up some modified form, but so far the property of hydrogen bonding is concerned it is not affected. Further from (III) it is also obvious that the chelation is between a secondary and a tertiary

vicinal hydroxyl and is entirely different from saturated ethyleneglycol or *O*-dihydroxybenzene type of compounds which do not give five or six-membered chelate rings.



(*b*) *Structural Relationship between Aconitine and Delphinine.*—The long-suspected constitutional relationship between aconitine and delphinine on the basis of the related botanical origin and the close resemblance in their chemical behaviour (Ann. Rep. Chem. Soc., 1944, **41,** 226 ; Jacobs and Craig, *J. Biol. Chem.*, 1939, **127,** 361 ; **128,** 431 ; 1941, **136,** 303) and physiological effects is greatly strengthened by common characteristics present in their infra-red spectra (Fieser and Fieser, "Natural Products related to Phenanthrenes", 1949, p. 618). The spectrum of aconitine includes all the delphinine bands, particularly in the region above 7.69 μ and also contains several additional strong bands near 9.62, 8.77 and 7.69 μ. These extra bands do not arise from any deep-seated structural differences between the two alkaloids. They are simply produced by the two hydroxyl groups which aconitine molecule contains in excess of delphinine.

Fig. 1
Infra-red absorption spectra.



(*c*) *A Non-conjugated double bond.*—A band at 5.95 μ in the spectrum of delphinine and near 5.89 μ in that of aconitine suggests the presence of a carbonyl group and/or a non-conjugated C=C group. But in the spectra of aconine and delphonine which do not contain a carbonyl group as a result of hydrolysis or $LiAlH_4$ -reduction of aconitine and delphinine, a strong band at 6.02 μ and 6.04 μ indicates the presence of a non-conjugated double bond; there is no band at 6.18—6.2 μ characteristic of the conjugated double bonds. Hence postulation of a conjugated system of double bonds by Jacobs (*J. Biol. Chem.*, 1944, **154**, 2931) in suggesting a hypothetical structure for alkamines is not well established.

(*d*) *Aliphatic ether linkage.*—A strong band at 9.17 μ in the spectra of delphinine and delphonine and that near 9.10 μ and 9.12 μ in the spectra of aconitine and aconine indicates an aliphatic ether, *i.e.* due to four methoxyl groups in each.

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A STUDY ON THE ISOLATION, PROPERTIES AND CHEMICAL COMPOSITION OF JUTE WAX

By W. G. Macmillan, A. B. Sen Gupta and A. Roy

Jute fibre has been found to contain a small amount of waxy substance (0.5-0.6%) as determined by extraction with an alcohol-benzene mixture, which represents only a small fraction (18%) of the original waxy components occurring in the bast portion of the plant. Of the different solvents studied for the complete extraction of wax from jute fibre with a minimum contamination of impurities, the conventional alcohol-benzene mixture appears to be the best. An analysis of the extract obtained with this mixed solvent indicates, however, that the material is associated with a high proportion of non-waxy substances. In course of purification of the crude wax, the non-waxy components have been separated into two distinct fractions and each found to be mainly of a resinous character. The purified wax, representing 40.2% of the original waxy substance, is low melting (m. p. 58-62°) and light brown in colour; it consists of fatty acids (33.0%), alcohols (47.3%), sterols (7.1%), hydrocarbons (9.7%) and inert matter (2.9%), the saturated and unsaturated acid contents being 29.1% and 3.9% respectively..

Similar to most other plant materials, jute possesses a thin layer of wax on the outer sheath of the epidermal cells of the stem, and this layer serves to prevent the plant from desiccation (Barker, *J. Text. Inst.*, 1939, **30**, P 274). It is probable therefore that the waxy coating is removed along with the epidermis during the usual biological methods of retting employed for isolation of the fibre. It is not, however, definitely known whether the wax retained by the isolated fibre actually occurs in the vascular fibre layer of the bast, thus remaining unaffected during retting or is derived from the remnant of epidermal layer owing to imperfect retting. Sarkar, Bandyopadhyay and Nodder (*Indian Central Jute Committee, Tech. Res. Mem.*, 1946, No. 6, 6) are of opinion that the comparatively high wax content of jute fibre, which has been stated to vary from 0.38% to 2.26%, originates partly from the presence of adherent non-fibrous tissue due to under-retting.

The natural wax content of jute fibre is usually determined by extracting the material with a mixture of alcohol-benzene (1 : 2, v/v) for 12 hours (Powrie and Speakman, *J. Text. Inst.*, 1943, **34**, T79), filtering the extract to eliminate any extraneous matter and small fibres and weighing the residue after removal of the solvent. The yield of wax (apparent value) obtained by this method, however, cannot be taken as the true wax content of the fibre since there is a possibility of the product being contaminated with other soluble impurities derived from jute.

The present investigation was initiated with the object of studying the properties and chemical composition of jute wax since very little information appears to be available on this subject. Although the work described has been mainly concerned with analysis of the wax obtained from jute fibre, it was considered of importance to also examine the effect of the usual biological retting method on the apparent wax content in order to determine the proportion of the original wax in the bast portion of the plant retained by the isolated fibre. Prior to isolating a sufficient quantity of wax for determining the properties, it was considered desirable to make a comparative study of the effect of different solvents on the apparent wax content in order to select a solvent for the complete extraction of wax from the fibre with a minimum of contamination. The usual alcohol-benzene mixture appeared to be suitable for the purpose, but subsequent analysis of the extract revealed that the material was highly contaminated with impurities. The crude wax was therefore fractionated by utilising its difference in solubility in different solvents with a view to isolating the wax in a less impure state, and two non-waxy fractions were eventually separated from the waxy components. The investigations were further extended to determine the physical and chemical constants of both the crude and purified wax, the chemical nature of the non-waxy fractions and the approximate composition of the purified wax.

EXPERIMENTAL

Two varieties of good quality jute fibre, *i.e.*, White and Tossa (obtained from Pakistan) were employed, the fibre being collected from the middle portion of the strands and cut to small pieces, approximately 6″ in length. The sample of crude wax used for studying the properties was isolated from a mixture of different varieties of fibre but what was subsequently purified was obtained from the white variety only. The bast sample used was obtained by mechanical separation from the plant stem.

Effect of Biological Retting on the Apparent Wax Content.—The air-dried sample of jute bast (100 g.) was kept immersed in tap water for 3 weeks when retting was found to be practically complete, and the isolated fibre after washing with water was air-dried. Both the unretted bast (10 g.) and the isolated fibre (20 g.) were extracted with alcohol-benzene mixture (1 : 2, v/v) in a soxhlet apparatus for 12 hours, at the rate of four extractions per hour, the extract filtered, dried at 100° and weighed, a mean of two determinations being taken ; the apparent wax contents of the bast and the fibre samples were found to be 1.47% and 0.47% (on the oven-dry material) respectively. Further, it was observed that the isolated fibre represented only 58% of the original bast. It appears therefore that the fibre retains only a small fraction (18%) of the waxy components occurring in the bast, the greater portion being eliminated during retting.

Effect of Extraction with Different Solvents on the Yield of Apparent Wax.—Several samples of jute fibre were extracted with different solvents as described above and the results obtained expressed as apparent wax contents, a mean of two determinations being noted. The results are shown in Table I.

TABLE I

Solvent.	Yield of apparent wax from		Solvent.	Yield of apparent wax from	
	White jute.	Tossa jute.		White jute.	Tossa jute.
Alcohol (absolute)	0.84	1.39	Benzene	0.41	0.32
Alcohol-benzene (1 : 2)	0.57	0.49	Chloroform	0.40	0.29
Acetone	0.52	0.26	Carbon tetrachloride	0.25	0.24
Ethyl ether	0.51	0.48	Petroleum ether (b.p. 40-60°)	0.22	0.16
Toluene	0.42	0.28			

Results are expressed as a percentage on the original oven-dry jute.

It is evident from Table I that the maximum yield of apparent wax is obtainable on extracting jute with alcohol, while alcohol-benzene gives a slightly lower, and carbon tetrachloride and petroleum ether, considerably lower values. The alcohol extract was clear under hot condition, but on cooling a white precipitate appeared and, in order to ascertain the total extractable material the solution was subjected to hot filtration ; the residue obtained after removal of the solvent was greenish brown in colour, which showed a red fluorescence in ultra-violet light, indicating the possible presence of chlorophyll. The colour of the alcohol-benzene extract was dark brown, while that of carbon tetrachloride or petroleum ether extract was somewhat lighter. It seems probable that the higher yield obtained with alcohol is attributable to the solubilising effect of this solvent on some component of jute other than wax and, in view of greater contamination of this product than that obtained with alcohol-benzene, it has been decided to employ the latter solvent for the isolation of a sufficient quantity of jute wax for the determination of physical and chemical properties and chemical composition.

Isolation of Crude Wax.—The alcohol-benzene extract, obtained from approximately 10,000 g. of jute fibre, was first heated in a steam oven, the material being occasionally stirred to remove the entrapped solvent and finally dried over fused calcium chloride *in vacuo*; the weight of the product obtained was approximately 50 g. The isolated wax was a dark brown, hard and brittle solid, partially soluble in benzene, carbon tetrachloride and petroleum ether.

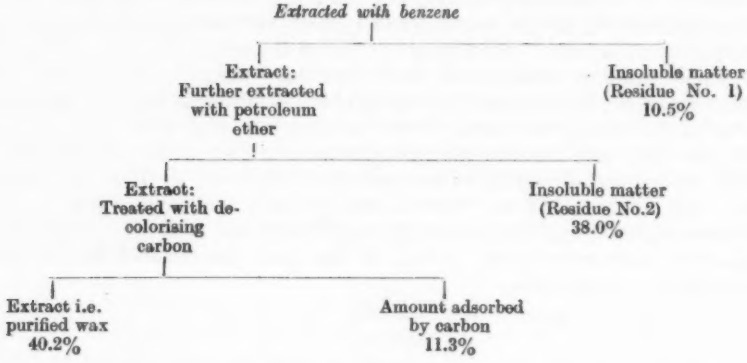
Since plant wax usually consists primarily either of esters of higher fatty acids and aliphatic alcohols or a mixture of esters, free acids and alcohols, with small quantities of hydrocarbons and sterols, the summation of fatty acids and unsaponifiable matter is expected to correspond very nearly to the original weight of the wax. If, however, the former is considerably lower than the latter, it will be obvious that the wax is not pure but is associated with impurities which have presumably been solubilised during isolation of the components. With a view to examining the purity of the isolated jute wax, an investigation was made to ascertain the fatty acid content and unsaponifiable matter of the sample, the determination being carried out according to the procedure employed by Tonn and Schoch (*Ind. Eng. Chem.*, 1946, **38**, 413). It was observed that the fatty acid content and unsaponifiable matter of the sample were 31.3% and 29.5% respectively and since the summation of these two components represented only 60.8% of the wax, the isolated jute wax appeared to exist in a highly impure state.

Purification of Crude Wax.—Another 50 g. of crude wax were isolated from jute fibre (white variety) by the procedure as described above and the material was next extracted with benzene in small lots for 12 hours when the major portion was solubilised leaving an insoluble matter (Residue No. 1). The extract on evaporation in a steam oven and drying over calcium chloride *in vacuo* gave a deep brown solid mass which on extracting again with petroleum ether for 12 hours yielded a considerable amount of insoluble substance (Residue No. 2). Since the waxy substance obtained from the ether extract was still brown in colour, the material (dissolved in benzene) was therefore further treated with decolorising carbon (J. T. Baker Chemical Co., America; using 1% on the weight of wax) in order to remove any associated colouring matter. The mixture was centrifuged and the residue washed with benzene to minimise the loss of wax due to adsorption; the wax which was then recovered from the combined liquor was found to be light brown in colour and soluble in alcohol, benzene, carbon tetrachloride and ether. Continuation experiments showed that treatments with acidic potassium dichromate or permanganate, gaseous chlorine and hydrogen peroxide practically failed to produce any further improvement in shade. The procedure used for purification of crude wax and the results obtained are summarised in Table II.

Properties of the Residues.—The residue No. 1 was a dark brown lustrous substance, while the residue No. 2 was somewhat dull greenish brown in colour. Both of these materials were amorphous and brittle in nature, mostly soluble in cold alcohol and readily in warm caustic soda with the formation of soap. When heated, the residues melted and the resulting products were found to be soluble in hot linseed oil. On heating the residue No. 2 and subjecting the product to steam distillation, small drops of oily substance were perceptible on the surface of the distillate. Since the amount of residue No. 1 was small it was not possible to examine this residue for the isolation of oily product. In addition, the residues were found to possess high acid and saponification values and low unsaponifiable matters. It appears likely therefore from the above properties that both of the residues are predominantly

resinous in character. The colour tests of the isolated jute resins were determined according to the procedures described by Mantell *et al.* ("The Technology of Natural Resins," 1942, p. 440), and the physical and chemical properties by Fryer and Weston ("Technical Handbook of Oils, Fats and Waxes," 1939, II, pp. 38-129). The results are given in Table III and Table IV.

TABLE II*


Crude wax
Extracted with benzene
Extract: Further extracted with petroleum ether
Insoluble matter (Residue No. 1) 10.5%
Extract: Treated with decolorising carbon
Insoluble matter (Residue No.2) 38.0%
Extract i.e. purified wax 40.2%
Amount adsorbed by carbon 11.3%

* Results are expressed as a percentage on crude wax.

The samples of resin isolated from jute are medium hard and the high acid value and solubility of the materials in both alcohol and linseed oil suggest that these substances approach more near to Manila resins (Mantell *et al.*, *loc cit.*, pp. 8, 771). The saponification value of the materials, however, is considerably higher than that of Manila. Further, the characteristic colour reactions of jute resins are somewhat different from those of the allied substances.

TABLE III

Properties.	Residue No. 1.	Residue No. 2.
Melting point*	85—87°	95—99°
Ash content (%)	0.25	0.65
Solubility in organic solvents	Soluble in alcohol, acetone; insoluble in benzene, carbon tetrachloride and solvent oil	Soluble in alcohol, acetone, benzene and carbon tetrachloride and practically insoluble in solvent oil
Acid value	104.6	89.8
Saponification value	266.7	261.5
Ester value	162.1	171.7
Unsaponifiable matter	2.9	6.4

* Determined by capillary method.

The isolated resins from jute did not appear to be in highly pure state, but contaminated with some impurities. The residue No. 2 gave positive fluorescence test for chlorophyll. Both the residues, No. 1 and No. 2, were found to be partially soluble in water, the solubility in boiling water being 10.0% and 7.4% respectively. In addition, the samples responded to the usual colour tests for lignin (Phloroglucinol and Mäule tests). When the materials were subjected to the process of isolating lignin by treatment with cold 72% sulphuric acid (Sen

Gupta and Callow, *J. Text. Inst.*, 1949, **40,** T650) large amounts of insoluble substance were left behind. These insoluble residues on being further reacted with acidic sodium chlorite solution, which is believed to exert a selective solubilising effect only on the lignin fraction (Chattopadhyay and Sarkar, *Proc. Nat. Sci., India*, 1946, **12,** 23), suffered small losses in weight, corresponding to 3.8% and 0.28% lignin on the residue No. 1 and No. 2 respectively.

TABLE IV

Colour reactions.	Residue No. 1.	Residue No. 2.
Libermann test	Dark brown	Yellowish brown
Halphen-Hicks test	Lilac-brown to pale reddish brown	Lilac-brown to deep reddish brown
Benzoyl chloride test		
(A)	Greenish brown	Green to greenish brown
(B)	Deep reddish brown	Red changing to deep reddish brown
Diazotized sulphanilic acid (coupled) in caustic potash	Deep reddish orange	Reddish orange
Sulphuric acid and ammonium molybdate	Brown with purple tinge	Brown with purple tinge

Properties of Crude and Purified Waxes.—The properties of the crude and purified waxes were determined by following mainly the procedures described by Fryer and Weston (*loc. cit.*). The results are shown in Table V.

TABLE V

Properties.	Crude wax.	Purified wax.	Properties.	Crude wax.	Purified wax.
Melting point	69-74°	58-62°	Ester value	66.3	76.5
Density (at 25°)	0.9975	0.9825	Iodine value*	27.4	32.8
Sapon. value	118.7	115.3	Acetyl value	158.4	57.5
Acid value	52.4	38.8			

* Determined with Hanus solution.

The values obtained from the crude and purified samples of wax (Table V) are not strictly comparable, because the materials have been isolated from different varieties of jute fibre. Nevertheless, the difference in acetyl values of the samples is very marked and it seems probable that the presence of resinous substances is mainly responsible for higher value of the crude wax. During the determination of density, it was observed that the appearance of the surface layer of the crude sample changed considerably in contact with water, while no such effect was noted with the purified material, and this was found to be due to a partial solubility (7.3%) of the former sample in water.

The purified wax is a comparatively low melting substance amongst the vegetable waxes. The high acetyl and acid values of the sample indicate that considerable proportions of free alcohol and fatty acids are associated in the wax.

Chemical Composition of Purified Wax.—On analysing the purified wax it was observed that the mixed fatty acids and unsaponifiable matter were 33.0% and 64.1% respectively, the unaccountable matter amounting to 2.9%, being likely to be attributable mainly to an inert colouring matter including any possible presence of glycol or glycerol. The colour of the isolated mixed fatty acids was very dark, while that of the unsaponifiable matter was light brown.

A quantitative separation of the unsaturated acids from the saturated components was effected by the usual lead salt method. The alcohols were determined from a portion of unsaponifiable matter (3 g.) by the procedure suggested by Cochenhausen (*J. Soc. Chem. Ind.*,

1897, 447) and the hydrocarbons (from 2 g. sample) by the method described by Warth ("The Chemistry and Technology of Waxes", 1947, p. 326). The sterol contents were then obtained by difference. A summary of the analytical results is reported in Table VI.

TABLE VI

Constituents of wax.	Amount.	M.P.
Saturated fatty acids	29.1%	72-75°
Unsaturated „ „	3.9	45-48°
Alcohols	47.3	58-60°
Sterols	7.1	—
Hydrocarbons	9.7	68-70°
Inert matter (unaccountable)	2.9	—

The colour of the saturated fatty acids was very dark, almost indistinguishable from that of the mixed fatty acids, while the unsaturated components were somewhat light brown in shade; both the alcohol and hydrocarbon fractions were pale brown in colour.

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5 : 6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT. PART V. SEPARATION OF CADMIUM FROM DIFFERENT ELEMENTS

By Anil Kumar Majumdar and Anil Kumar De

The reagent 5 : 6-benzoquinaldinic acid may be used for the estimation of cadmium and its separation from tartrate, phosphate, arsenate, vanadate, tungstate, molybdate, alkaline earths, silver, mercury, lead, beryllium, thorium, zirconium, uranium, rare earths, iron, aluminium, chromium, titanium, bismuth, antimony and tin either by the proper control of p_H or by the use of complexing agents.

In previous communications (this *Journal*, 1952, **29**, 255, 499 ; 1953, **30**, 123, 401 ; *Anal. Chim. Acta*, 1953, **9**, 529) it was shown that the reagent 5 : 6-benzoquinaldinic acid could be used for the gravimetric estimation of copper, cadmium, zinc, manganese, nickel and cobalt and for the colorimetric estimation of iron which forms a red inner—metallic complex, highly soluble in alkali cyanide solution with intensification of colour.

During the estimation of cadmium and its separation from copper (*loc. cit.*) it was observed that the reagent precipitated the cadmium completely over the p_H range 3.12 to 9.40.

The cadmium salt precipitated at p_H 3.12 to 3.85 was highly crystalline and of compositions $Cd(C_{14}H_8NO_2)_2$, 1.5 H_2O at 105-110° and $Cd(C_{14}H_8NO_2)_2$ at 125°-130°, and that at a p_H higher than 3.85 should be dried at a temperature over 165° to anhydrous salt before weighing as it retained 1.5 to 2 molecules of water even at 125°-130°.

The purpose of the present investigation is to show that 5 : 6-benzoquinaldinic acid behaves as a selective reagent for the estimation of cadmium in presence of tartrate, phosphate, arsenate, molybdate, vanadate, tungstate, alkaline earths, silver, mercury, lead, beryllium thorium, zirconium, uranium, rare-earths, iron, aluminium, chromium, titanium, bismuth, antimony and tin.

The separation of cadmium from alkaline earths, phosphate, arsenate, vanadate, molybdate and tungstate has been done by the simple control of p_H.

Thiourea keeps silver in solution; potassium iodide, mercury; ammonium acetate, lead; while thorium, zirconium, uranium, rare-earths, iron, aluminium, chromium, titanium, bismuth, antimony, tin and beryllium are kept in solution in presence of tartrate.

Experimental

Reagent grade chemicals were used always except where otherwise mentioned. Besides the reagents and standard solutions described in previous papers (*loc. cit.*) ammonium acetate, thiourea (B.D.H.—L.R.) and potassium iodide were the other chemicals used in this work.

An 1 % solution of sodium benzoquinaldinate (1 g. of recrystallised 5 : 6-benzoquin-

aldinic acid, of m.p. 187°, per 100 c.c. of the solution) was used as a precipitant and for every experiment the amount of the reagent added was about five times the amount of cadmium present.

Analytical Procedure.—For the separation of cadmium from silver, the slightly acidic solution was treated with thiourea (2 g.) and then after dilution to 200 c.c. and heating to boiling, the cadmium was precipitated and estimated by the usual procedure (*loc. cit.*). Instead of thiourea, potassium iodide (2 g.) was used when cadmium was separated from mercury. From both silver and mercury it could also be separated by adding first an excess of potassium iodide and then an excess of thiourea.

Separation from lead was done in presence of an excess of ammonium acetate (2 g.) after acidification with acetic acid.

Beryllium, thorium, zirconium, uranium, rare-earths, iron, aluminium, chromium, titanium, bismuth, antimony and tin were kept in solution, while cadmium was precipitated from the solution containing about 2-4 g. of tartrate and rendered ammoniacal. Weakly acid solution with tartrate also kept thorium, uranium, and zirconium in solution.

Separation from vanadate, molybdate and tungstate could easily be done from ammoniacal solution.

Alkaline earths did not interfere when cadmium was precipitated from solutions acidified with acetic or mineral acid. Barium and strontium in larger amounts coprecipitate. To prevent this, maintaining the p_H, the total volume of the solution should be increased to increase the solubility of their salts.

Phosphate and arsenate also did not interfere in presence of mineral acids.

TABLE I

No.	Metals taken.		p_H.	Cadmium salt.	Cadmium found.
1.	Cd Ag	13.18 mg. 236.50	3.70	65.3 mg.	13.19 mg.
2.	Cd Ag	65.90 14.19	3.80	327.0	66.05
3.	Cd Hg	13.18 105.90	5.42	65.2	13.17
4.	Cd Hg	65.90 7.06	5.80	327.2	66.09
5.	Cd Pb	13.18 100.80	5.20	65.2	13.17
6.	Cd Pb	65.90 7.20	5.16	326.6	65.97

TABLE II

No.	Metals taken.		p_H.	Cadmium salt.	Cadmium found.
1.	Cd	9.89 mg.	8.42	49.1 mg.	9.92 mg.
	Be	40.60			
2.	Cd	10.23	6.50	50.6	10.22
	Be	73.10			
3.	Cd	13.18	8.70	65.2	13.17
	Th	93.00			
4.	Cd	10.23	3.45	50.6	10.22
	Th	62.00			
4.	Cd	9.89	3.46	49.0	9.90
	Zr	67.60			
6.	Cd	10.23	6.55	50.6	10.22
	Zr	96.60			
7.	Cd	13.18	8.60	65.3	13.19
	U	101.20			
8.	Cd	10.23	3.54	50.6	10.22
	U	50.60			
9.	Cd	13.18	8.20	65.2	13.17
	Fe	97.20			
10.	Cd	10.23	6.36	50.7	10.24
	Fe	97.20			
11.	Cd	13.18	7.40	65.2	13.17
	Al	94.80			
12.	Cd	10.23	6.38	50.7	10.24
	Al	94.80			
13.	Cd	13.18	7.90	65.1	13.15
	Cr	97.00			
14.	Cd	10.23	6.18	50.7	10.24
	Cr	97.00			
15.	Cd	10.23	7.65	50.6	10.22
	Ti	92.00			
16.	Cd	8.18	7.20	40.4	8.16
	Ti	103.60			
17.	Cd	10.23	6.12	50.7	10.24
	Bi	46.24			
18.	Cd	10.23	6.30	50.6	10.22
	Bi	231.20			
19.	Cd	10.23	6.65	50.8	10.26
	Sb	190.90			
20.	Cd	10.23	6.38	50.6	10.22
	Sb	381.80			
21.	Cd	10.23	7.55	50.7	10.24
	Sn	270.40			
22.	Cd	10.23	7.24	50.5	10.20
	Sn	405.60			
23.	Cd	10.23	8.50	50.7	10.24
	ΣR_2O_3	281.80			
24.	Cd	10.23	9.30	50.6	10.22
	ΣR_2O_3	427.20			

TABLE III

No.	Metals taken.		p_H.	Cadmium salt.	Cadmium found.
1.	Cd	9.89 mg.	9.52	49.0 mg.	9.90 mg.
	V	97.00			
2.	Cd	26.36	9.40	130.5	26.36
	V	32.31			
3.	Cd	13.18	9.10	65.3	13.19
	Mo	40.32			
4.	Cd	13.18	9.28	65.2	13.17
	Mo	134.40			
5.	Cd	10.23	8.85	50.6	10.22
	W	45.92			
6.	Cd	10.23	9.20	50.7	10.24
	W	114.80			

TABLE IV

No.	Metals taken.		p_H.	Cadmium salt.	Cadmium found.
1.	Cd	10.23 mg.	3.28	50.7 mg.	10.24 mg.
	Ca	180.40			
2.	Cd	10.23	3.18	50.6	10.22
	Ca	360.50			
3.	Cd	10.23	3.28	52.4	10.58
	Sr	362.80			
4.	Cd	10.23	3.36	50.7	10.24
	Sr	362.80			
5.	Cd	10.23	3.42	54.8	11.07
	Ba	450.60			
6.	Cd	10.23	3.50	50.8	10.26
	Ba	450.60			

* Total volume of the solution was 400 c.c.

TABLE V
Cadmium = 10.68 mg.

No.	Ions taken.		p_H.	Cadmium salt.	Cadmium found.
1.	P_2O_5	169.8 mg.	3.4	52.6 mg.	10.63 mg.
2.	P_2O_5	135.8	—	53.0	10.70
3.	As_2O_5	173.5	3.5	52.8	10.66
4.	As_2O_5	216.9	—	52.9	10.68

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ANALOGUES OF PTEROYLGLUTAMIC ACID. PART I. REPLACEMENT OF *p*-AMINOBENZOIC ACID BY *p*-AMINOSALICYLIC ACID

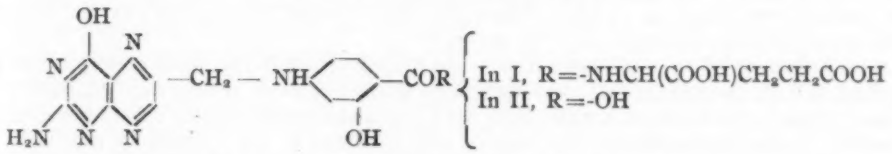
By PRABHAT RANJAN PAL

The analogues of pteroylglutamic acid and pteroic acid were synthesised by substituting *p*-aminosalicylic acid in place of *p*-aminobenzoic acid in the main molecules. The analogues were found to be antagonistic to pteroylglutamic acid when tested on *streptococcus faecalis* R.

After the synthesis of pteroylglutamic acid by Angier and co-workers (*Science*, 1946, **103**, 667) various structural analogues of pteroylglutamic acid and pteroic acid have been synthesised and studied in respect of their biological activity and have been reviewed by Hutchings (*Vitamins & Hormones*, 1948, **6**, 1), Jukes (*Ann. N. Y. Acad. Sci.*, 1950, **52**, 1336) and Petering (*Physiol. Rev.*, 1952, **32**, 197). Most of the compounds so far synthesised have been shown to antagonise the action of pteroylglutamic acid when tested on certain species of micro-organisms, specially *Lactobacillus casei* and *Streptococcus faecalis* R. which require pteroylglutamic acid for their growth, and can produce folic acid deficiency, when administered to animals such as mice, chicken, monkey and human being.

The possible use of pteroylglutamic acid antagonists in the treatment of leukemia (Farber, *New England J. Med.*, 1948, **238**, 787) has led us to the present investigation for the synthesis of more potent antagonists of the parent compound.

The present paper describes the synthesis of N[4-(N-{(2-amino-4-hydroxy-6-pteridyl)-methyl}-amino)-salicylyl]-*l* (+)-glutamic acid (I) and 4-(N-{(2-amino-4-hydroxy-6-pteridyl)-methyl}-amino)-salicylic acid (II) by substituting *p*-aminosalicylic acid in place of *p*-aminobenzoic acid in the molecules of pteroylglutamic acid and pteroic acid respectively.



The methods of Waller *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 19) and Boothe *et al.* (*ibid.*, 1948, **70**, 1099) were followed with slight modifications for the synthesis of the analogues in which 2 : 4 : 5-triamino-6-hydroxypyrimidine sulphate, 2 : 3-dibromopropionaldehyde and the appropriate aromatic amine were condensed together at an acid p_H. One half equivalent of sodium dichromate was added during the condensation. The *p*-aminosalicylyl-*l* (+)-glutamic acid was synthesised by reducing the corresponding nitro compound with ammonium sulphide in aqueous solution. The starting material, 4-nitrosalicylic acid, was prepared according to Bhate *et al.* (*Proc. Ind. Acad. Sci.*, 1949, **29 A**, 196). 2 : 3-Dibromopropionaldehyde was prepared (Moureu and Boismenu, *Ann. chim.*, 1921, *ix*, **15**, 209) by bromination of acrolein in carbon tetrachloride solution. For the synthesis of 2 : 4 : 5-triamino-6-hydroxypyrimidine, the corresponding 5-nitroso derivative was reduced with zinc dust and hydrochloric acid (Traube, *Ber*, 1900, **33**, 1371 ; Pal, this *Journal*, 1954, **31**, 673).

The crude analogues were purified by following the method previously described (Pal, *loc. cit.*). The ultraviolet absorption spectra of the pure compounds in 0.1*N*-NaOH and 0.1*N*-HCl solutions were determined in the Beckman spectrophotometer Model DU, and the absorption maxima and minima in mμ of the compounds are recorded in Table I. The absorption spectrum of compound (I) in 0.1*N*-HCl did not show any sharp inflection. The

alkaline permanganate oxidation products of the analogues were isolated according to Seeger *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 1753) and their identities were established by comparing their ultraviolet absorption spectra with those of the same authentic compound, 2-amino-4-hydroxypteridine-6-carboxylic acid†. This reaction also proves that the side chain in the pteridine ring is attached to the 6-position.

TABLE I

U.V. absorption data and inhibition index of the pteridines.

Wave-lengths in mμ.

Compound.	0.1*N*-NaOH				0-1*N*-HCl		Inhibition index.
	Max.		Min.		Max.	Min.	
(I)	232	325	—	310	—	—	280
(II)	251	357	230	301	315	271	20,000

Effects of these synthetic analogues on the growth of *Streptococcus faecalis* R. were investigated. They were found to exercise certain inhibitory effect on the particular microorganism in the presence of pteroylglutamic acid. The values for inhibition index for half maximum inhibition at the concentration of 0.005 microgram of pteroylglutamic acid per 10 ml. are shown in Table I. The details of the microbiological assay are being published elsewhere.

*EXPERIMENTAL

Acetyl-4-nitrosalicylic Acid.—The procedure followed was similar to that of Viscontini and Pudles (*Helv. Chim. Acta*, 1950, **33**, 591). The product after recrystallisation from a mixture of benzene and petroleum ether (40°—60°) gave colorless needles, m.p. 148°. Viscontini reported the m.p. as 155°; Bhate (*loc. cit.*) reported the m.p. as 144.5°. (Found: N, 6.27. Calc. for $C_9H_7O_6N$: N, 6.22 per cent).

4-Nitrosalicylyl-l (+)-glutamic Acid.—The preceding acid (1.75g., 0.008 mole) was taken in a flask and dry benzene (40 ml.) and redistilled thionyl chloride (2 ml.) were added to this. The mixture was heated on a water-bath for 5 hours and excess solvent was removed under suction at that temperature. The residue was dissolved in dry dioxane (5 ml.) and the solution was added dropwise during half an hour to a mixture of *l* (+)-glutamic acid (1.2 g., 0.008 mole) and magnesium oxide (1.1g., 3×0.008 mole) in water with stirring, and at a temperature of 0°. After acid chloride was added to the mixture, it was stirred for another half an hour at 0° and allowed to stand at room temperature (30°) for another hour. The solution was filtered and acidified with HCl to Congo red while cooling with ice, when a light yellow precipitate separated out. The mixture was kept at 5° overnight and filtered. The yield was 1.3 g. A second crop (0.75 g.) of the material was obtained by concentrating the filtrate on the water-bath to a small volume and then cooling. The total crude product was purified by extracting with minimum quantity of water on the water-bath and cooling the extract to 0° when the desired product (1.8 g.) of m.p. 160° was obtained. During the period of condensation and recrystallisation the acetyl group was knocked off (cf. Jensen and Linholt, *Acta Chem. Scand.*, 1949, **3**, 205). The substance was finally purified by recrystallisation from dioxane, benzene and petroleum ether (60°—80°) mixture when the m.p. rose to 169°. (Found: C, 46.22; H, 4.03; N, 8.84. $C_{12}H_{12}O_8N_2$ requires C, 46.14; H, 3.87; N, 8.97 per cent).

†Kindly supplied by the Lederlie Laboratories Division of American Cynamid Co., New York.
*All melting points are uncorrected.

N-[4-(N-{(2-*amino*-4-*hydroxy*-6-*pterydyl*)-*methyl*}-*amino*)-*salicylyl*)-1(+)-*glutamic Acid* (I). —The above glutamic acid (3.12 g., 0.01 mole) was dissolved in 6*N*-NH_4OH (16 ml.) and the solution was saturated with H_2S under cooling. The solution was heated on the water-bath for 1 hour when most of the excess H_2S escaped and sulphur separated out. This was then filtered and acidified with glacial acetic acid and again filtered. This solution gave positive Bratton-Marshall reaction and was used directly for the condensation.

2 : 4 : 5-Triamino-6-hydroxypyrimidine sulphate (2.57 g., 0.01 mole) was dissolved in water (300 ml.) containing hydrated sodium acetate (2 g.) by heating to 80°. This solution was added to the solution containing the amine and the p_H was adjusted to 3-4 with 5*N*-HCl. The solution was stirred while 2 : 3-dibromopropionaldehyde (2.16 g.) in acetic acid (5 ml.) and sodium dichromate (0.49 g.) in water (10 ml.) were added simultaneously for half an hour, the temperature being maintained at 50° and p_H between 3 and 4 during the reaction period. After the addition of dibromopropionaldehyde the mixture was stirred for another hour at room temperature (30°) and kept at 5° overnight. The crude material was filtered, washed with water, alcohol and acetone. It weighed 3.55 g.

The crude material was purified by following the method previously described (Pal, *loc. cit.*) when a dark brown microcrystalline material was obtained. The substance had no definite m.p., it charred above 300°. (Found : C, 45.93 ; H, 4.01 ; N, 19.27. $C_{19}H_{19}O_7N_7,2H_2O$ requires C, 46.25 ; H, 3.88 ; N, 19.87 per cent).

The U.V. absorption spectra of 10 mg./litre solution of the substance (I) in 0.1*N*-NaOH and 0.1*N*-HCl were determined in 1 cm. cell with a Beckman spectrophotometer Model DU and the absorption maxima and minima in mμ are shown in Table I. The compound (I) did not show any sharp inflection in 0.1*N*-HCl solution.

The compound (I) on alkaline permanganate oxidation yielded 2-amino-4-hydroxypteridine-6-carboxylic acid whose identity was established by comparison of the U.V. absorption curve with that of an authentic sample.

4-(N-{(2-*amino*-4-*hydroxy*-6-*pteridyl*)-*methyl*}-*amino*)-*salicylic Acid* (II).—2 : 4 : 5-Triamino-6-hydroxypyrimidine sulphate (10 g.) was dissolved in water (1000 ml) containing hydrated sodium acetate (10 g.) at 80°. To this was added, *p*-aminosalicylic acid (12 g.) dissolved in water (200 ml.) containing HCl (conc., 10 ml.) and the p_H was adjusted to 3-4 with 5*N*-NaOH. To this solution 2 : 3-dibromoproionaldehyde (15.3 g.), dissolved in 95% alcohol (900 ml.), was added slowly with stirring within one hour, while the p_H was maintained at 3-4 and the temperature was adjusted between 40°and 50°. The mixture was further stirred for one and half hours and allowed to stand at 5° for another 12 hours. It was then filtered and the cake was washed with water, alcohol and acetone, and dried. The yield was 10.6 g. It was purified by following the same method as described previously. Two grams of the crude product gave 70 mg. of the pure product. The analytical sample was dried at 100°/1 mm. (Found : C, 50.97 ; H, 3.89 ; N, 25.40. $C_{14}H_{12}O_4N_6$ requires C, 51.22 ; H, 3.69 ; N, 25.60 per cent).

The U.V. absorption maxima and minima in mμ of the substance (II) in solutions containing 10 mg./litre in 0.1*N*-NaOH and 0.1*N*-HCl are shown in Table I.

The compound (II) on alkaline permanganate oxidation gave 2-amino-4-hydroxypteridine-6-carboxylic acid which was identified by comparing the U.V. absorption spectra with that of an authentic sample.

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HYDROXYFLUOFERRIATES. PART I. HYDROXYFLUOFERRIATES OF Na, K, Ni, Zn AND Cd

By GRIHAPATI MITRA

A new hydroxyfluoride complex of trivalent iron has been isolated. The fluorine atoms of the hexafluoride and the pentafluoride iron have been replaced by the hydroxyl group. Thus like the hydroxyfluoborate, hydroxyfluoroberyllate and hydroxyfluorostannate, another new hydroxyfluoro complex has been established. In the present paper only the sodium salt of the monohydroxy pentafluoferriate has been described. The monohydroxy tetrafluoferriates of metals, *i.e*, those of sodium, potassium, zinc, nickel and cadmium, have been isolated and their properties studied. The potassium salt crystallises with half a molecule of water. Both the sodium salts that are formed are anhydrous. Zinc, nickel and cadmium salts crystallise with seven and six molecules of water. The compounds are in general more soluble than the ordinary hexafluoride and the pentafluoride complexes. Some of the salts are deliquescent. It has been proved by X-ray analysis that the replacement of the fluorine atom by the hydroxyl group does not alter the crystal lattice to any appreciable extent.

Till now only three elements are known to yield hydroxyfluoride complexes, viz., boron (Meerwein, *Ber.*, 1933, **66,** 411; Wamser, *J. Amer. Chem. Soc.*, 1948, **70,** 1209), tin (Briggs, *Z. anorg. Chem.*, 1913, **82,** 441) and beryllium. It has been discussed by the author (this *Journal*, 1955, **32**, 61) that the stability of the hydroxyfluoride complexes might be even greater than the fluoride complexes. This fact has been proved in the case of beryllium (*loc. cit.*). In this connection it may be mentioned that it has also been observed that the partial replacement of hydroxyl group by a chlorine atom increases the stability of the resulting hydroxychloride complex (Scholder and Patsch, *Z. anorg. Chem.*, 1934, **217,** 214).

In view of the fact that iron also forms very stable fluoride complexes an attempt has been made for the preparation of the hydroxyfluoride complexes of iron as well. The fluoride complexes of divalent iron are few in number. All attempts to isolate the hydroxyfluoride complexes of divalent iron ended in the precipitation of the hydroxide of iron. Iron in the hexavalent state forms complexes directly with oxygen, viz., the ferrates. No fluoride complex of hexavalent iron is known. The maximum number of fluoride complex is known with trivalent iron (Remy and Busch, *Ber.*, 1933, **66,** 961). In this higher state of oxidation iron is less basic than in the divalent state and for this reason there is every possibility of the formation of hydroxyfluoride complexes without precipitating the insoluble hydroxide.

The present paper deals with the preparation and properties of the hydroxyfluoride complexes of trivalent iron.

EXPERIMENTAL

Trivalent iron forms three types of complexes with fluorine : (1) FeF_4^-; (2) FeF_5^{2-}; (3) FeF_6^{3-}. Remy and Busch (*loc. cit.*) have made a thorough study of these complexes and it has been verified both experimentally and theoretically that the pentafluoride complex is the most stable one. The members of the magnesium-copper group of metals form a well-defined series of salts with the pentafluoferriate group. These salts may be represented by the general formula, $M^{II}FeF_5$, $7H_2O$.

In the course of the present investigation we have been able to isolate the maximum number of compounds where it has been possible to substitute the hydroxyl group by the fluorine atom of the pentafluoferriate group. The fluorine atom of the hexafluoferriate

group has been replaced by the hydroxyl group in one compound only. The methods of preparation and properties of these hydroxyfluoride complexes are given below. The standard methods of analysis were followed.

Sodium Monohydroxy Pentafluoferriate.—Freshly precipitated ferric hydroxide was just dissolved in the minimum quantity of hydrofluoric acid. Addition of the acid should preferably be stopped while the solution remains just turbid. It was filtered and to the filtrate sodium fluoride solution in the molecular proportion of 1:3 was added with constant stirring. The solution at once became turbid due to the formation of the insoluble sodium salt. This was heated on a water-bath for about fifteen minutes when the compound settled down. This was then filtered and washed with 60% alcohol. The compound was dried in a vacuum desiccator over sulphuric acid. (Found: Na, 29.00 ; Fe, 23.52 ; F, 39.58. Calc. for Na_3FeF_5OH : Na, 29.13 ; Fe, 23.58 ; F, 40.11 per cent).

The sodium salt is sparingly soluble in water and cannot be recrystallised. A saturated solution of hydroxyfluoferriate becomes turbid by the addition of a few drops of dilute hydrofluoric acid. Sodium fluoferriate is obviously formed and this is even less soluble than the hydroxyfluoferriate. The X-ray diffraction diagram of this compound reveals that the substitution of hydroxyl group by a fluorine atom does not alter the crystal lattice to any appreciable extent.

Sodium Monohydroxy Tetrafluoferriate.—Freshly precipitated ferric hydroxide and sodium carbonate were taken in the molecular proportion of 1 : 2. Dilute hydrofluoric acid was then added and the mixture heated in a platinum basin on a water-bath. The addition of hydrofluoric acid was continued for about two hours and was stopped when the solution became just turbid and white crystals were formed at the bottom. This was thoroughly shaken with cold water and the supernatant liquid containing ferric hydroxide was removed. Washing was repeated several times till the compound became free from contaminated ferric hydroxide. The compound was dried and analysed. (Found : Na, 23.31 ; Fe, 28.48 ; F, 38.96. Na_2FeF_4OH requires Na, 23.60 ; Fe, 28.66 ; F, 38.91 per cent).

The magnetic susceptibility of the compound was found to be almost the same as that of the ordinary complex fluoride of iron. The solubility of the salt is higher than that of sodium pentafluoferriate. It cannot also be recrystallised.

Potassium monohydroxy tetrafluoferriate half hydrate was prepared exactly in the same way as the corresponding salt of sodium. (Found : K, 32.88 ; Fe, 23.48 ; F, 32.19. $K_2FeF_4OH,\frac{1}{2}H_2O$ requires K, 33.13 ; Fe, 23.66 ; F, 32.20 per cent).

The solubility of the salt is greater than the corresponding salt of pentafluoride complex and the compound could not be recrystallised.

Zinc Monohydroxy Tetrafluoferriate Heptahydrate.—A solution of a weighed quantity of ferrous sulphate was boiled with a few drops of nitric acid for about ten minutes. By the addition of sodium hydroxide solution iron was precipitated as ferric hydroxide. This was filtered and the precipitate was washed free of alkali. An equimolecular quantity of zinc fluoride was taken in a platinum basin containing about 75 c.c. water. The ferric hydroxide was added to it and the mixture was heated on an asbestos board over a low flame. Dilute hydrofluoric acid was then added cautiously till the solution remained just brownish owing to the presence of traces of undissolved ferric hydroxide. This was filtered and the filtrate was kept in a refrigerator. Colourless crystals appeared after a few hours. This was filtered washed with 60% alcohol and dried in air. (Found : Fe, 16.26 ; Zn, 18.99 ; F, 21.96. $ZnFeF_4OH, 7H_2O$ requires Fe, 16.40 ; Zn, 19.21 ; F, 22.33 per cent).

The compound loses one molecule of water at about 80°. It is slightly deliquescent.

Zinc Monohydroxy Tetrafluoferriate Hexahydrate.—The filtrate, mentioned as above, was treated with alcohol at the ordinary temperature instead of keeping in a refrigerator. Colorless crystals appeared. They were filtered, washed with alcohol and dried in air. (Found : Fe, 17.00 ; F, 22.99. $ZnFeF_4OH$, $6H_2O$ requires Fe, 17.32 ; F, 23.58 per cent).

The compound begins to lose water at about 100°. The last traces of water were, however, removed only with difficulty.

Nickel Monohydroxy Tetrafluoferriate Heptahydrate.—Equimolecular quantities of ferric hydroxide and nickel carbonate were dissolved in the minimum quantity of hydrofluoric acid which was added during two and half hours. The solution was heated on an asbestos board. The presence of a little excess of ferric hydroxide is beneficial. After filtration the filtrate was kept in a refrigerator when beautiful pale green crystals appeared. These were filtered, washed with alcohol and analysed. (Found : Fe, 16.51 ; F, 22.50. $NiFeF_4OH$, $7H_2O$ requires Fe, 16.74 ; F, 22.78 per cent). The compound is deliquescent.

Nickel monohydroxy terafluoferriate hexahydrate was precipitated from a solution of nickel the preceding tetrafluoride ferriate by the addition of alcohol at ordinary temperature. The precipitate assumed crystalline structure after about five minutes. The microscopic crystals were filtered, washed with alcohol and analysed. (Found : F, 24.08. $NiFeF_4OH$, $6H_2O$ requires F, 24.12 per cent). The compound loses water above 100°.

Cadmium monohydroxy tetrafluoferriate heptahydrate was prepared exactly in the same way as above. When the solution was allowed to crystallise at ordinary temperature the heptahydrated salt was obtained. (Found : Cd, 28.68 ; Fe, 14.40 ; F, 19.73. $CdFeF_4OH$, $7H_2O$ requires Cd, 29.00 ; Fe, 14.42 ; F, 19.62 per cent).

The compound loses one molecule of water at nearly 70°. At 140° almost the total amount of water escaped and the compound probably decomposed at that temperature. The salt is highly soluble in water and appreciably deliquescent.

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STUDIES IN LESS FAMILIAR OXIDATION STATES. PART I. ARGENTIC OXIDE : A NEW METHOD OF PREPARATION

By R. L. Dutta

Alkaline hypochlorite has been shown to oxidise Ag_2O to AgO. Large excess of hypochlorite and somewhat higher temperature favour oxidation but heating for a long period brings about some decomposition.

The higher oxides of silver have so far been obtained by three main methods. Anodic oxidation of concentrated and neutral solution of silver nitrate gives insoluble $Ag_7O_{11}N$ (Watson, *J. Chem. Soc.*, 1906, **89**, 578 ; Mulder and Heringa, *Rec. trav. chim.*, 1900, **15**, 1 ; Tanatar, *Z. anorg. Chem.*, 1901, **28**, 331). Treatment of this oxynitrate complex with boiling water results in pure AgO. A black oxide is also formed when solutions of $AgNO_3$ and $K_2S_2O_8$ are mixed. Austin (*J. Chem. Soc.*, 1911, **99**, 262) reported it to be Ag_4O_4. This precipitate was later investigated by Yost (*J. Amer. Chem. Soc.*, 1926, **48**, 152) and also by Carman (*Trans. Faraday Soc.*, 1934, **30**, 566) who showed that the silver was first precipitated as Ag_2O_3 which on standing finally changed to $Ag_2O_3.2AgO$. Recently, Barbieri and Malaguti (*Atti Accad. Lincei*, 1950, **8**, 619) have obtained AgO by oxidising $AgNO_3$ with alkaline persulphate. Jirsa and Jellinek (*Z. anorg. Chem.*, 1926, **61**, 158) obtained Ag_2O_3 by the action of dry ozone on powdered silver.

The purpose of the present work was to investigate the action of alkaline hypochlorite on Ag_2O. A study of the solubilities of Ag_2O and AgCl shows the former to be comparatively insoluble. Besides, prolonged heating of AgCl in alkaline medium is known to give Ag_2O. Thus, an attempt towards oxidising Ag_2O by NaOCl seemed worthwhile.

Experimental

Preliminary investigations indicate that for appreciable oxidation higher temperature and also higher concentration of hypochlorite have to be employed. Hence optimum amount of NaOCl was first determined.

NaOH (35-37 g.) was dissolved in water (50 c.c.) and the solution cooled. Chlorine was bubbled through this solution till the weight increased by the desired amount. During chlorination the solution was kept stirred and the temperature was maintained below 20°. Precipitated NaCl was then filtered off through a glass funnel. $AgNO_3$ (1 g.) was dissolved in water (10 c.c.), NaOH (5-6 g.) added, followed by the freshly prepared NaOCl solution. The whole was then heated to 60°-65° on a water-bath and maintained there for an hour with good stirring. (In about 15 minutes, the brown colour of the Ag_2O changed to greyish black). The contents were then cooled down to room temperature and filtered through a glass funnel. While on the filter the product was washed free of alkali with plenty of water. Portions of the wet sample were removed and analysed for the ratio of active oxygen to total silver.

Analyses were done by adding a portion of the wet sample to a known excess of acidified (dil. H_2SO_4) ferrous sulphate and then backtitrating the excess ferrous with standard $KMnO_4$. In the same solution total silver was determined by KSCN method. The wet oxide was highly reactive, liberating no active oxygen during analysis, whereas the dried samples were indifferent.

In Table I are recorded data showing improved oxidation with increasing amounts of NaOCl. AgCl impurities in the preparations were computed from analyses on the dried samples.

TABLE I

Influence of hypochlorite concentration on the purity of AgO.

Increase in wt. after chlorination.	Ratio of active O : total Ag in the wet sample.	AgCl impurity.
2 g.	0.804	4.79%
4	0.938	0.78
8	0.944	1.00

The optimum amount of NaOCl for 1 g. of $AgNO_3$ would thus appear to be 8 g. Further, the ratio of active O to total Ag (which should be 2 for Ag_2O_3 and 1 for AgO) approaches 1, showing that alkaline hypochlorite oxidises Ag_2O to AgO state.

Influence of Temperature and Duration of Heating on Purity.—The influence of temperature and duration of heating were studied with a view to increasing the purity of the oxide. Data are recorded in Table II.

TABLE II

Increase in wt. after chlorination = 8g.

Temp.=50°—55°.			Temp.=60°—65°.		
Duration of heating.	Active O. / Total Ag	Remarks.	Duration of heating.	Active O. / Total Ag	Remarks.
15 min.	0.198	Too much AgCl; very little reactive.	15 min.	0.593	Enough AgCl; not so reactive.
30 min.	0.697	Still enough AgCl; reactive.	30 min.	0.878	Practically no AgCl; highly reactive.
			1 hr.	0.943	,, ,,
1 hr.	0.871	Still enough AgCl; more reactive.	2 hrs.	0.888	,, ,,
2 hrs.	0.896	Very little AgCl; more reactive.	Temp.=75°-80°.		
			15 min.	0.897	,, ,,
			30 min.	0.925	,, ,,
			1 hr.	0.973	,, ,,
			2 hrs.	0.903	,, ,,

It is thus evident that higher temperature enhances oxidation but heating for a long time results in some decomposition. Higher temperature has another influence in that it practically does away with the main bulk of the AgCl impurity and makes the oxide more reactive. Most favourable conditions of preparation are thus a temperature of 75°-80° and maintenance of this for an hour. Sample thus prepared analysed for AgO, 96.6%; Ag_2O, 2.4%; AgCl, 1%.

The dried samples did not react quantitatively with ferrous sulphate in dilute H_2SO_4 medium, much active oxygen being evolved. Thus in one case, the ratio of active O to total Ag in wet and dry varieties of the same preparation was 0.973 and 0.845 respectively. Suitable methods of direct analysis of these dried samples are yet to be developed.

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CHALKONES. PART III. PREPARATION OF CHALKONES FROM 2-HYDROXY-4-METHOXY-5-NITRO-ACETOPHENONE (5-NITROPEANOL), THEIR BROMINATION AND STUDY OF THE REACTIVITY OF CHALKONE DIBROMIDES

By V. G. Kulkarni and G. V. Jadhav

2-Hydroxy-4-methoxy-5-nitro-acetophenone has been condensed with benzaldehyde, salicylaldehyde, 2-hydroxy-3 : 5-dibromobenzaldehyde, 2-methoxybenzaldehyde, 2-methoxy-5-bromobenzaldehyde, anisaldehyde, 3-bromo-4-methoxybenzaldehyde, vanillin and 5-bromovanillin, and the chalkones formed have been brominated. The chalkone dibromides gave back chalkones with potassium iodide, coumaranone derivatives with caustic potash, sodium ethoxide, borax and dimethylaniline, and flavones with potassium cyanide. With pyridine they gave α-bromochalkones.

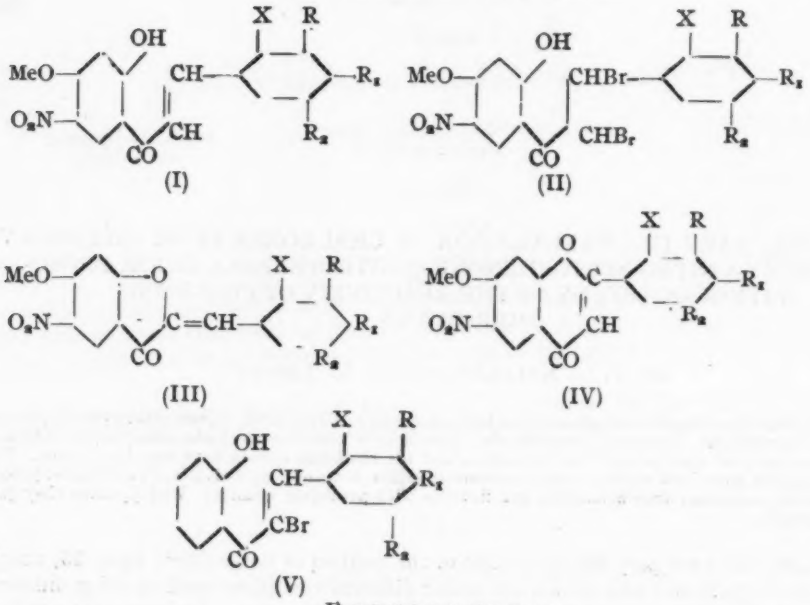
The chalkones were prepared according to the method of Sorge (*Ber.*, 1902, **35,** 1069). Bromination of chalkones was carried out under different conditions such as using different quantities of bromine in acetic acid solution and with liquid bromine. In acetic acid medium bromine always added at the double bond, except in the case of the chalkone from salicylaldehyde when excess of bromine solution gave a compound with bromine in the aldehyde nucleus also. With liquid bromine, however, bromine was found to enter the aldehyde part as well as its addition to the double bond, except in the case of the benzaldehyde-chalkone, where only addition took place. Under no circumstances bromine entered the ketonic nucleus due to the methylation of one of the hydroxy groups and due to the presence of the nitro group attached to the nucleus (cf. Kulkarni and Jadhav, this *Journal*, 1954, **31,** 763).

The reactivity of the dibromides was examined with potassium iodide, potassium hydroxide, sodium ethoxide, borax, dimethylaniline, potassium cyanide and pyridine. Potassium iodide gave chalkones whose constitutions were proved by their synthesis (Dodwadmath and Wheeler, *Proc. Ind. Acad. Sci.*, 1935, **2A**, 438 ; Barne and Payton, *J. Amer. Chem. Soc.*, 1936, **58**, 1300 ; Nadkarni, Warrior and Wheeler, *J. Chem. Soc.*, 1937, 1798 ; Vandrewalla and Jadhav, *J. Univ. Bombay*, 1948, **16,** 43).

In the case of potassium hydroxide, sodium ethoxide, borax and dimethylaniline, they gave coumaranone derivatives (Vandrewalla and Jadhav, *loc. cit.*) which gave red coloration with sulphuric acid. With pyridine, the dibromide gave α-bromochalkones (cf. Bhagwat and Wheeler, *J. Chem. Soc.*, 1939, 94 ; Vandrewalla and Jadhav, *Proc. Ind. Acad. Sci.*, 1948, **28A**, 125 ; Nadkarni, Warrior and Wheeler, *loc. cit.*).

With alcoholic potassium cyanide, the dibromides gave flavones (cf. Hutchins and Wheeler, *J. Chem. Soc.*, 1939, 91 ; Vandrewalla and Jadhav, *loc. cit.*).

Formation of these different products clearly shows that the reactivity of the dibromides is greatly influenced by the presence of the groups in the ketonic part, for simple methylation of one of the hydroxy groups alters the course of the reaction with pyridine and potassium cyanide (cf. Kulkarni and Jadhav, *loc. cit.*).



(I) (II) (III) (IV) (V)

EXPERIMENTAL

These chalkones (I) were prepared by dissolving the requisite ketone (5 g.) and aldehyde (3.5 c.c. in the case of liquids and 3.5 g. in the case of solids) in presence of 50% KOH solution in 50% EtOH (100 c.c.) and allowing the reaction to proceed for 6 to 7 days. The following new compounds have been obtained (Table I).

TABLE I

Compounds having structure (I).

R=	R_1=	R_2=	X=	M.P.	Crystallised from.	Mol. formula.	Analysis. Found.	Calc.
H	H	H	H	179-80°	Acetic acid	$C_6H_{13}O_5N$	N, 4.8%	4.7%
H	H	H	OH	230°	,,	$C_{16}H_{13}O_6N$	N, 4.7	4.4
Br	H	Br	OH	250°	Nitrobenzene & acetic acid	$C_{16}H_{11}O_6NBr_2$	Br, 34.1	33.8
H	H	H	OMe	164-65°	Acetic acid	$C_{17}H_{15}O_6N$	N, 4.1	4.3
H	H	Br	OMe	187-88°	,,	$C_{17}H_{14}O_6NBr$	Br, 19.3	19.6
H	OMe	H	H	160-61°	,,	$C_{17}1H_{15}O_6N$	N, 4.0	4.3
Br	OMe	H	H	184-85°	,,	$C_{17}1H_{14}O_6NBr$	Br, 19.3	19.6
OMe	OH	H	H	162-63°	EtOH	$C_{17}H_{15}O_7N$	N, 4.1	4.06
OMe	OH	Br	H	206-207°	Acetic acid	$C_{17}H_{14}O_7NBr$	Br, 18.7	18.8

Dibromides (II) were prepared by brominating the chalkones (I, 1g.) in acetic acid medium for 1 hour with acetic acid solution of bromine (10%) (when 12 c.c. gave dibromides and 24 c.c. gave tetrabromo derivatives) or with liquid bromine (5 c.c.) for 1 day at room temperature in the case of compounds marked with an asterisk (*). The products were isolated in the usual way and described in Table II.

TABLE II

Dibromides (II).

R=	R_1=	R_2=	X=	M.P.	Crystallised from.	Mol. formula.	% Bromine. Found.	Calc.
H	H	H	H	220°	Acetic acid	$C_{16}H_{13}O_5NBr_2$	34.9	34.8
H	H	H	OH	130°	,,	$C_{16}H_{13}O_6NBr_2$	33.3	33.6
Br	H	Br	OH	150°	,,	$C_{16}H_{11}O_6NBr_4$	50.9	50.5
H	H	H	OMe	110-11°	Alcohol	$C_{17}H_{15}O_6NBr_2$	33.1	32.7
H	H	Br	OMe	116-17°	,,	*$C_{17}H_{14}O_6NBr_3$	42.5	42.2
H	OMe	H	H	84-85°	Alcohol	$C_{17}H_{15}O_6NBr_2$	32.4	32.7
Br	OMe	H	H	178-79°	Acetic acid	*$C_{17}H_{14}O_6NBr_3$	41.8	42.2
OMe	OH	H	H	110-11°	Alcohol	$C_{17}H_{15}O_7NBr_2$	31.5	31.7
OMe	OH	Br	H	116-17°	,,	*$C_{17}H_{14}O_7NBr_3$	41.2	41.09

Action of Potassium Iodide.—The dibromide was boiled with an equal weight of potassium iodide in presence of acetone for 4 hours and this led to the regenaration of the chalkone.

Action of Potassium Hydroxide.—The dibromides (II, 1 g.) were mixed with 10% KOH solution (10 c.c.) and the mixture boiled for about 10 minutes. The products obtained on acidification were crystallised from acetic acid in all cases. They are coumaranone derivatives (III). They gave red coloration with sulphuric acid. They are described in Table III.

TABLE III

Coumaranone derivatives (III).

R=	R_1=	R_2=	X=	M.P.	Mol. formula.	Analysis. Found.	Calc.
H	H	H	H	229-30°	$C_{16}H_{11}O_5N$	N, 5.0%	4.7%
H	H	H	OH	214-15°	$C_{16}H_{11}O_6N$	N, 4.8	4.5
Br	H	Br	OH	195-96°	$C_{16}H_9O_5NBr_2$	Br, 34.0	33.9
H	H	Br	OMe	167-68°	$C_{17}H_{12}O_6NBr$	Br, 19.8	19.7
H	OMe	H	H	250-51°	$C_{17}H_{13}O_6N$	N, 4.3	4.3
Br	OMe	H	H	179-80°	$C_{17}H_{12}O_6NBr$	Br, 19.8	19.7
OMe	OH	H	H	209-10°	$C_{17}H_{13}O_7N$	N, 4.5	4.1
OMe	OH	Br	H	195-96°	$C_{17}H_{12}O_7NBr$	Br, 18.7	18.95
H	H	H	OMe	149-50°	$C_{17}H_{13}O\ N$	N, 4.4	4.3

Action of Sodium Ethoxide.—The chalkone dibromides (II, 1 g.) were mixed with ethyl alcohol (25 c.c.) and sodium ethoxide solution (25 c.c.) (prepared from 0.15 g. of sodium) and the mixture was boiled for 4 hours, acidified and crystallised from acetic acid. Coumaranones (III) were obtained.

Action of Borax.—The chalkone dibromides (1 g.) were mixed with alcohol (15 c.c.) and borax (3 g.) dissolved in water (15 c.c.) and the mixture was heated on a boiling water-bath for about 4 hours and worked up as above. Coumaranones (III) were obtained.

Action of Dimethylaniline.—The chalkone dibromides (II, 1 g.) were mixed with alcohol (25 c.c.) and dimethylaniline (10 c.c.) and the mixture was heated on a boiling water-bath for about 4 hours, acidified and worked up as above. Coumaranones (III) were obtained.

TABLE IV

Flavones (IV).

R=	R_1=	R_2=	X=	M.P.	Mol. formula.	Analysis. Found.	Calc.
H	H	H	H	180°	$C_{16}H_{11}O_2N$	N, 5.0%	4.7%
H	H	H	OH	229-30°	$C_{16}H_{11}O_6N$	N, 4.4	4.5
Br	H	Br	OH	214-15°	$C_{16}H_9O_3NBr_2$	Br, 34.2	33.9
H	H	H	OMe	164-65°	$C_{17}H_{13}O_6N$	N, 4.4	4.3
H	H	Br	OMe	202-203°	$C_{17}H_{12}O_6NBr$	Br, 19.7	19.7
H	OMe	H	H	254-65°	$C_{17}H_{13}O_6N$	N, 4.4	4.3
Br	OMe	H	H	Above 310°	$C_{17}H_{12}O_6NBr$	Br, 20.0	19.7
OMe	OH	H	H	199-200°	$C_{17}H_{13}O_7N$	N, 4.4	4.1
OMe	OH	Br	H	Above 300°	$C_{17}H_{12}O_7NBr$	Br, 18.6	18.95

TABLE V

Bromostyryl ketones (V).

R=	R_1=	R_2=	X=	M.P.	Mol. formula.	% Bromine. Found.	Calc.
H	H	H	H	252-53°	$C_{16}H_{12}O_2NBr$	21.2	21.1
H	H	H	OH	219-20°	$C_{16}H_{12}O_6NBr$	20.4	20.3
Br	H	Br	OH	209-10°	$C_{16}H_{10}O_6NBr_3$	43.8	43.4
H	H	H	OMe	215-16°	$C_{17}H_{14}O_6NBr$	19.6	19.6
H	H	Br	OMe	182-83°	$C_{17}H_{13}O_6NBr_2$	32.3	32.8
H	OMe	H	H	256-57°	$C_{17}H_{14}O_6NBr$	19.6	19.6
Br	OMe	H	H	116-17°	$C_{17}H_{13}O_6NBr_2$	32.5	32.8
OMe	OH	H	H	260-61°	$C_{17}H_{14}O_7NBr$	18.7	18.8
OMe	OH	Br	H	199-200°	$C_{17}H_{13}O_7NBr_2$	31.4	31.8

Action of Potassium Cyanide.—The dibromides (II, 1 g.) were mixed with rectified spirit (40 c.c.) and potassium cyanide (1 g.) and the mixture was heated on a boiling water-bath for 45 minutes. It was worked up as above. Flavones (IV) were obtained. They gave yellow coloration with sulphuric acid. They are described in Table IV.

Action of Pyridine.—The chalkone dibromides (II) were boiled for 5 minutes with pyridine (10 c.c.), acidified and crystallised from acetic acid. α-Bromostyryl ketones (V) were obtained. They are described in Table V.

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IONIC EQUILIBRIA IN SOLUTION. PART I. CADMIUM ACETATE IN AQUEOUS SOLUTION

By S. Bardhan and S. Aditya

The solubility of cadmium oxalate in sodium acetate at 35° has been studied. The higher solubility of cadmium oxalate in sodium acetate than in potassium nitrate solution (which has also been determined) indicates the formation of $CdAc^+$ ion. The constant for the equilibrium, $CdAc^+ \rightleftharpoons Cd^{2+} + Ac^-$, has been calculated.

From the electromotive force studies, it was reported that cadmium acetate in solution was not completely dissociated. The ionic equilibrium can be represented as

$$CdAc_2 \rightleftharpoons CdAc^+ + Ac^-$$
$$\Downarrow\Uparrow$$
$$Cd^{2+} + Ac^-$$

In the present work the solubility of cadmium oxalate in sodium acetate solution has been measured. The aim in view is to see if this can throw some light on the nature of cadmium acetate in solution and how far the results agree with those obtained by other methods.

Experimental

Cadmium oxalate was prepared according to Clayton and Vosburgh (*J. Amer. Chem. Soc.*, 1937, **59**, 244). The solubility of the salt in water at 25° was $3.018 \times 10^{-4} M$. The oxalate content of a vacuum-dried sample was 99.8% of the theoretical.

A stock solution of sodium acetate and acetic acid (p_H 4.7) was prepared by mixing the required amounts of acetic acid and caustic soda. Potassium nitrate solution was prepared from Kahlbaum *pro analysi* sample, dried in an air oven at 95°.

The solubility of cadmium oxalate in sodium acetate solution as well as potassium nitrate solution at 35° was determined by titrating 100 c.c. of the filtrate with $N/50$-$KMnO_4$ solution which was standardised every day against Analar sodium oxalate, dried at 120°. Each experiment was done in duplicate which agreed within 2%. The mean values are shown in Table I.

Table I

Solubility of cadmium oxalate in sodium acetate and potassium nitrate solutions at 35°.

Conc. of salt.	log s in NaAc.	log s in KNO_3.	log s_o^2/s.	log $(s-s_o^2/s)$.	log $f_{Cd^{2+}}$	$K \times 10^2$.
0.01 *M*	$\bar{4}.7330$	$\bar{4}.6300$	$\bar{4}.5270$	$\bar{4}.3102$	$\bar{1}.7924$	1.295
0.02	$\bar{4}.7890$	$\bar{4}.6700$	$\bar{4}.5510$	$\bar{4}.4142$	$\bar{1}.7482$	2.018
0.04	$\bar{4}.9428$	$\bar{4}.7250$	$\bar{4}.4872$	$\bar{4}.7556$	$\bar{1}.6902$	1.785
0.05	$\bar{4}.9609$	$\bar{4}.7324$	$\bar{4}.5099$	$\bar{4}.7745$	$\bar{1}.6721$	2.113
0.06	$\bar{3}.0017$	$\bar{4}.7505$	$\bar{4}.4991$	$\bar{4}.8379$	$\bar{1}.6484$	2.183
0.08	$\bar{3}.0603$	$\bar{4}.7864$	$\bar{4}.5125$	$\bar{4}.9157$	$\bar{1}.6233$	2.495
0.10	$\bar{3}.1309$	$\bar{4}.8146$	$\bar{4}.4983$	$\bar{3}.0157$	$\bar{1}.5911$	2.455
0.12	$\bar{3}.1476$	$\bar{4}.8356$	$\bar{4}.4236$	$\bar{3}.0298$	$\bar{1}.5682$	2.839
0.15	$\bar{3}.2269$	$\bar{4}.8622$	$\bar{4}.4969$	$\bar{3}.1373$	$\bar{1}.5378$	2.745

Mean value of equilibrium constant (K) = 1.990×10^{-2}.

Discussion

Experimental results show that the solubility of cadmium oxalate in sodium acetate is higher than that in potassium nitrate solution. Since cadmium nitrate may be taken to be completely dissociated (this *Journal*, 1953, **30**, 217) the change in solubility of cadmium oxalate in potassium nitrate is due to the change in ionic strength. So the higher solubility of cadmium oxalate in sodium acetate solution is due to interaction between cadmium and acetate ions. If n acetate ions combine with one cadmium ion, then the equilibrium may be represented as $Cd^{2+}+nAc^- \rightleftharpoons CdAc_n^{-(n-2)}$. The value of K can be found out in the following way. Putting the concentration terms the equilibrium constant is given by

$$K = \frac{[Cd^{2+}]\,[Ac^-]^n}{[CdAc_n]}.$$

The concentration of cadmium ion is given by the expression $[Cd^{2+}]=s_o^2/s$, where 's_o' is the solubility of cadmuim oxalate in pure water and s, that in sodium acetate solution.

$$[CdAc_n]=[\text{Oxalate}]-[Cd^{2+}]=s - s_o^2/s.$$

The concentration of acetate may be taken to be equal to that of sodium acetate.

$$K = \frac{s_o^2/s\,[Ac^-]^n}{s-s_o^2/s}.$$

Therefore Taking logarithm and rearranging,

$$\log [Ac^-] = \tfrac{1}{n}\{\log(s-s_o^2/s)-\log s_o^2/s\} + \tfrac{1}{n}\log K.$$

When log $[Ac^-]$ is plotted against $\{\log(s-s_o^2/s)-\log s_o^2/s\}$, a linear curve is obtained and the slope of the curve is unity, which indicates that one acetate ion reacts with one cadmium ion. The intercept of the curve gives an approximate value of K. The equilibrium constant K can be evaluated in the following way after taking the inter-ionic attraction into account.

If s be the solubility of cadmium oxalate in sodium acetate solution and s_o, the solubility in potassium nitrate solution of the same concentration, then $[Cd^{2+}]=s_o^2/s$, assuming that the ionic strength of sodium acetate solution is but little affected as a result of solubility of cadmium oxalate. Hence

$$[CdAc^+] = [\text{Oxalate}]_{\text{total}} - [Cd^{2+}].\,[Ac^-]$$

has been taken to be equal to that in sodium acetate solution. K will be given by the expression,

$$K = \frac{[Cd^{2+}]\,f_{Cd^{2+}}\,[Ac^-]\,f_{Ac^-}}{[Cd\,Ac^+]\,f_{Cd\,Ac^+}} = \frac{[Cd^{2+}]\,[Ac^-]\,f_{Cd^{2+}}}{[Cd\,Ac^+]},$$

if we assume $f_{Ac^-}=f_{Cd\,Ac^+}$. Column 4 of the table gives the value of $[Cd^{2+}]$, column 5 that of $[CdAc^+]$. The value of K has been calculated assuming that $f_{Cd^{2+}}=f_{Ba^{2+}}$ at the same ionic strength. Calculated values of K are given in column 7. The mean value is 1099×10^{-2}.

While comparing the conclusions of this experiment with those from the E.M.F. measurements, it is found that here the presence of only one species viz., $CdAc^+$, is indicated. This may be due to the limitation of the solubility method. The first stage of dissociation of cadmium acetate is fairly high, K being 1×10^{-1}. For

$$Cd\,Ac_2 \rightleftharpoons CdAc^+ + Ac^-$$

E.M.F. measurements give the degree of dissociation as 0.915 at 0.02 M and 0.74 for 0.1 M. At 0.01 M, even E.M.F. measurements could not detect incomplete dissociation (this *Journal*, 1953, **30**, 255). It may be pointed out here that investigation by solubility

method in case of lead acetate by Edmonds and Birnbaum (*J. Amer. Chem. Soc.*, 1940, **62**, 2367) showed the presence of $PbAc^+$ only. Earlier qualitative migration experiments by Noyes and Whitcomb (*Proc. Amer. Chem. Soc.*, 1905, **27**, 747) and also E.M.F. measurements from this laboratory (this *Journal*, 1952, **29**, 169) showed the presence of undissociated $PbAc_2$.

However, while concluding it may be said that although the solubility measurements could not show the presence of the undissociated $CdAc_2$ in our present case, it definitely confirms the conclusion as to the presence of $CdAc^+$ in solution.

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IONIC EQUILIBRIA IN SOLUTION. PART II.

ZINC ACETATE IN AQUEOUS SOLUTION

By S. Bardhan and S. Aditya

From the measurement of solubility of zinc oxalate in sodium acetate solution and the E.M.F. of the cell of the type, $Hg,Hg_2Ac_2 \mid Zn\,Ac_2 \parallel \parallel BaAc_2 \mid Hg_2Ac_2, Hg$, at 35°, the nature of zinc acetate in solution has been studied. The results obtained by both the methods indicate that the equilibrium for zinc acetate in solution can be represented as $ZnAc_2 \rightarrow ZnAc^+ + Ac^-$. The equilibrium constant for the reaction $ZnAc^+ \rightleftharpoons Zn^{2+} + Ac^-$ calculated from the solubility measurement is 2.6×10^{-2} and from the E.M.F. measurement, 3.45×10^{-2}. The agreement is fairly good in view of the limitations of the experimental technique.

Zinc and cadmium resemble each other very much in the chemical behaviour. Both have a tendency of auto-complex formation. In case of cadmium acetate, it was found that cadmium acetate was not completely dissociated (this *Journal*, 1953, **30**, 255). In the present work some investigations have been made about the ionic state of zinc acetate in solution. The solubility of zinc oxalate in sodium acetate solution and the E.M.F. of the cells of the type, $Hg,Hg_2Ac_2 \mid BaAc_2 \parallel \parallel ZnAc_2 \mid Hg_2Ac_2,Hg$, have been measured for the purpose.

Experimental

Zinc oxalate was prepared in the same way as described by Vosburgh and Clayton (*J. Amer. Chem. Soc.*, 1937, **59**, 244).

Sodium acetate stock solution (p_H about 6.7) was prepared by adding the required amount of acetic acid and caustic soda solution.

The solubility of zinc oxalate in sodium acetate solution was determined at 35° by titrating 100 c.c. of the solution with $N/50$ permanganate solution which was standardised against sodium oxalate. Column 3 of Table I shows the solubility of zinc oxalate in potassium nitrate solution and column 2, that in sodium acetate solution.

Table I

Solubility of zinc oxalate in sodium acetate and potassium nitrate solutions at 35°.

Conc. of salt.	log s in NaAc.	log s_0 in KNO_3	log s_0^2/s.	log $(s-s_0^2/s)$.	$f_{Zn^{2+}}$.	$K\times10^2$.
0.01 *M*	$\bar{4}.3371$	$\bar{4}.2727$	$\bar{4}.2083$	$\bar{5}.7466$	0.620	1.792
0.02	$\bar{4}.3881$	$\bar{4}.8284$	$\bar{4}.1815$	$\bar{5}.9708$	0.560	1.820
0.04	$\bar{4}.4320$	$\bar{4}.2988$	$\bar{4}.1656$	$\bar{5}.0934$	0.490	2.315
0.05	$\bar{4}.4815$	$\bar{4}.3018$	$\bar{4}.1221$	$\bar{4}.2321$	0.470	1.825
0.06	$\bar{4}.4832$	$\bar{4}.3118$	$\bar{4}.1404$	$\bar{4}.2204$	0.445	2.221
0.08	$\bar{4}.5272$	$\bar{4}.3358$	$\bar{4}.1444$	$\bar{4}.2952$	0.420	2.374
0.10	$\bar{4}.5400$	$\bar{4}.3658$	$\bar{4}.1916$	$\bar{4}.2817$	0.390	3.170
0.12	$\bar{4}.5726$	$\bar{4}.3828$	$\bar{4}.1930$	$\bar{4}.3381$	0.370	3.179
0.15	$\bar{4}.6313$	$\bar{4}.3977$	$\bar{4}.1641$	$\bar{4}.4346$	0.345	2.776
0.20	$\bar{4}.6799$	$\bar{4}.4551$	$\bar{4}.2303$	$\bar{4}.4896$	0.315	3.467

For the E.M.F. work, the stock zinc acetate solution was prepared by dissolving B.D.H. reagent quality zinc acetate in water containing acetic acid in order to prevent hydrolysis of the salt. The p_H of the solution was measured by means of a Marconi p_H meter and was found to be 4.22. The zinc content of the solution was estimated by the ammonium phosphate method.

A stock barium acetate solution was prepared by dissolving Merck's barium acetate in double distilled water. Calculated amount of acetic acid was added to the solution before dilution, so as to make the p_H of the barium a etate solution the same as that of the zinc acetate solution.

The experimental arrengement for E.M.F. measurements is similar to that employed earlier in the study of cadmium acetate solution (*loc. cit.*). The duplicate measurements agree within 0.2 mv. The E.M.F. readings are recorded in column 2 of Tables II and III.

TABLE II

Hg, Hg_2Ac_2	$ZnAc_2(c)$	Half satd. KCl bridge	$BaAc_2(c)$	Hg_2Ac_2, Hg.		
Conc. of $ZnAc_2$ & $BaAc_2$.	E.M.F.	Mean E.M.F.	Activity of acetate ion.	α.	Ionic strength.	$K\times10^4$.
0.01 *M*	0.0020 volt	0.0021 volt	0.0158	0.835	0.0267	4.95
	0.0021					
0.02	0.0033	0.0033	0.0285	0.736	0.0494	4.50
	0.0032					
0.04	0.0051	0.0052	0.0501	0.604	0.0883	3.98
	0.0052					
0.06	0.0066	0.0066	0.0700	0.552	0.1260	4.23
	0.0065					
0.08	0.0077	0.0077	0.0847	0.431	0.1489	3.04
	0.0076					
0.10	0.0089	0.0089	0.0987	0.352	0.1706	2.45
	0.0088					
0.12	0.0095	0.0095	0.1142	0.322	0.1973	2.41
	0.0093					

TABLE III

Hg, Hg_2Ac_2	$ZnAc_2(c)$	Satd. KCl bridge	$BaAc_2(c)$	Hg_2Ac_2, Hg.		
Conc of $ZnAc_2$ & $BaAc_2$.	E.M.F.	Mean E.M.F.	Activity of acetate ion	α	Ionic strength.	$K\times10^4$.
0.01 *M*	0.0020 volt	0.0021 volt	0.0157	0.835	0.0267	4.95
	0.0021					
0.02	0.0034	0.0034	0.0291	0.728	0.0509	4.59
	0.0033					
0.04	0.0055	0.0055	0.0497	0.593	0.0874	3.78
	0.0054					
0.06	0.0070	0.0070	0.0673	0.481	0.1177	3.04
	0.0069					
0.08	0.0084	0.0083	0.0826	0.387	0.1419	2.45
	0.0083					
0.10	0.0095	0.0095	0.9658	0.319	0.1632	2.07
	0.0094					
0.12	0.0102	0.0101	0.1008	0.284	0.1882	1.95
	0.0100					

DISCUSSION

A comparison of the solubility data in columns 2 and 3 of Table I shows that the solubility of zinc oxalate in sodium acetate is higher than that in potassium nitrate solution. If it is taken that there is no interaction between Zn^{2+} ion and NO_3^- ion, the variation of solubility is due to the effect of ionic strength. So the higher solubility in case of sodium acetate solution must be due to the interaction between Zn^{2+} and Ac^- ions.

If 'n' acetate ions associate with one Zn^{2+} ion, then the equilibrium in solution will be represented as

$$Zn^{2+} + nAc \longrightarrow ZnAc_n^{-(n-2)}.$$

The dissociation constant of the ionic equilibrium of the complex $ZnAc_n^{-(n-2)}$ will be given by

$$K = \frac{(Zn^{2+})\,(Ac^-)^n}{(ZnAc^{-(n-2)})}.$$

Putting concentration for the activity terms, by way of approximation, and analysing the results as has been done in our previous communication (this *issue*, *p.* 102), it is seen that one Ac^- ion combines with one Zn^{2+} ion. So the equilibrium is $Zn^{2+} + Ac^- \rightleftharpoons ZnAc^+$ and the equilibrium constant K will be given by the following expression, if the activity coefficient of Ac^- is taken to be equal to that of the $ZnAc^+$ ion.

$$K = \frac{[Zn^{2+}]\,[Ac^-]\,f_{Zn^{2+}}}{[ZnAc^+]}.$$

The concentrations of the Zn^{2+} and $ZnAc^+$ ions have been calculated in the same way as has been done in the case of cadmium acetate (*loc. cit*). The concentration of Ac^- ion has been taken equal to the concentration of sodium acetate in solution and $f_{Zn^{2+}}$ equal to $f_{Ba^{2+}}$. They are shown in Table I. The equilibrium constant K has been calculated in the same way as in case of cadmium acetate and the values are recorded in column 7 of Table I. The mean value of K is 2.6×10^{-2}.

Now coming to the consideration of the experimental results of the E.M.F. measurements, we find that the E.M.F. of the cells of the type studied is given by the equation,

$$E = 2.303\,\frac{RT}{F}\log_{10}\frac{a'_{Ac^-}\text{ in } BaAc_2}{a''_{Ac^-}\text{ in } ZnAc_2} + \epsilon$$

where ϵ is the liquid junction potential. This may be taken to be negligible since saturated and half saturated KCl solutions have been used as the bridge solution. Both the series of experimental readings (with saturated KCl and half saturated KCl as bridge solutions) have been treated separately for calculation. This has been done with a view to ascertaining how much the uneliminated liquid junction potential might vitiate the results so far as the value of the equilibrium constant is concerned.

If barium acetate dissociates completely, we have

$$E = 2.303\,\frac{RT}{F}\log_{10}\frac{c_1 f_1\text{ in } BaAc_2}{a_{Ac^-}\text{ in } ZnAc_2}$$

where c_1 and f_1 are the molar concentration and activity coefficient of Ac^- ion in barium acetate solution. Taking the activity coefficient of Ac^- ion to be equal to that of Cl^- ion in solutions having the same ionic strength, the activity of Ac^- in $ZnAc_2$ solution is found using the above equation. The values of a_{Ac^-} for different concentrations of zinc acetate are shown in column 4 of Tables II and III.

It may be assumed that zinc acetate dissociates according to the scheme :

$$ZnAc_2 \xrightarrow{\text{complete}} ZnAc^+ + Ac^-$$
$$\downarrow\uparrow$$
$$Zn^{2+} + Ac^-$$

The activity of the Ac^- ion in zinc acetate is $(1+\alpha)\, c\, f_{Ac^-}$. Now the activity of Ac^- in zinc acetate solution is known from the E.M.F. value. So using this value and equating this with $(1+\alpha)c, f_{Ac^-}$, the value of α is calculated by the method of approximation as has been done in our previous communications. Thus, the value of α for each concentration has been calculated. In Table III column 5 are given α values, calculated from the E.M.F. values with saturated KCl bridge solution and in column 5 of Table II, α for half-saturated KCl bridge solution. Column 6 of Tables II and III records the respective ionic strengths. Now considering the above scheme of equilibrium we have,

$$K_T = \frac{a_{Zn^{2+}} \times a_{Ac^-}}{a_{ZnAc^+}}$$

where K_T is the thermodynamic equilibrium constant, $a_{Zn^{2+}}$, a_{Ac^-} and a_{ZnAc^+} are the activities of Zn^{2+}, Ac^- and $ZnAc^+$ ions respectively. On substitution of the values of $a_{Zn^{2+}}$, a_{Ac} and $_{ZnAc^+}$ we

$$K = \frac{\alpha c\, f_{Zn^{2+}} \times (1+\alpha) c f_{Ac^-}}{(1-\alpha)\, c\, f_{ZnAc^+}} = \frac{(1+\alpha)\alpha c}{(1-\alpha)} f_{Zn^{2+}}, \text{ if } f_{Ac} = f_{ZnAc^+}$$

have, To evaluate K_T, $f_{Zn^{2+}}$ is to be known. For this the activity coefficient of zinc has been taken to be equal to that of Ba^{2+} ion at the same ionic strength. Now it is seen that for the same concentration of zinc acetate, we have slightly different values of α (calculated from readings with different bridge solutions) and this would give different ionic strengths for the same solution. However, the solution is the same and as such the ionic strength must be equal. So for ionic strength, we have taken the mean of the ionic strengths as were obtained by calculation from the E.M.F. readings. Thus knowing $f_{Zn^{2+}}$, α and c, the equilibrium constant K has been calculated. The values of K are shown in column 7 of Tables II and III. The mean value of K with saturated KCl and half-saturated KCl bridges are 3.26×10^{-2} and 3.65×10^{-2} respectively. The agreement between the values of K for any of the bridges used is fairly good. This justifies our assumption that the liquid junction potential has been eliminated for all practical purposes and can be neglected. The mean value of K is 3.45×10^{-2}.

When we compare the results obtained from the solubility measurement of zinc oxalate in sodium acetate solution with that from the E.M.F. measurements, we find that the presence of $ZnAc^+$ is indicated in both cases. The values of equilibrium constant are, however, 3.45×10^{-2} and 2.6×10^{-2} by E.M.F. and solubility methods respectively. This difference is possibly due to the limitation of the accuracy that can be or has been achieved in the two methods so far as experimental errors and assumptions in calculation are concerned. However, the order is the same and the agreement may be taken to be fairly good.

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IONIC EQUILIBRIA IN SOLUTION. PART III. COBALT ACETATE IN AQUEOUS SOLUTION

By S. Bardhan and S. Aditya

The nature of cobalt acetate in aqueous solution has been investigated by electromotive force measurement of the cells of the type, $Hg, Hg_2Ac_2 \mid NaAc(m') \parallel \begin{matrix}\text{Salt} \\ \text{bridge}\end{matrix} \parallel \begin{matrix}NaAc\ (m') \\ Co(NO_3)_2\ (m)\end{matrix} \mid Hg_2Ac_2, Hg$. The result indicates that cobalt acetate in solution is not completely dissociated. The ionic equilibrium is: $CoAc_2 \rightarrow CoAc^+ + Ac^-$, $Co^{2+} + Ac^-$

The constant for the equilibrium: $CoAc^+ \rightleftharpoons Co^{2+} + Ac^-$ has been calculated. The mean value is 3.65×10^{-2} at 35°.

Cobalt acetate is isomorphous with acetates of nickel and zinc. In the case of nickel it has been found that in solution nickel acetate exists (Jena, Aditya and Prasad this *Journal*, 1953, **30**, 633) as

$$NiAc_2 \longrightarrow NiAc^+ + Ac^-$$
$$\Downarrow\Uparrow$$
$$Ni^{2+} + Ac^-$$

A similar observation has been reported in the case of zinc acetate. In the present work the cells of the type

$$Hg, Hg_2Ac_2 \mid NaAc(m') \parallel \begin{matrix}NaAc(m') \\ Co\ (NO_3)_2(m)\end{matrix} \mid Hg_2Ac_2, Hg.$$

have been studied in order to have an idea about the nature of cobaltous acetate in solution.

Experimental

A stock solution (0,5206*M*) of cobalt nitrate was prepared from extrapure E. Merck sample in double distilled water. The exact concentration of cobalt was found by estimating cobalt by the thiocyanate method (Vogel, "Quantitative Analysis", p. 323). The p_H of the solution, as measured with the Marconi p_H meter, was 5.82.

A stock solution of sodium acetate having p_H 5.80 was prepared by mixing the required amounts of caustic soda and acetic acid solutions.

The solutions containing cobalt nitrate and sodium acetate were made by mixing definite volumes of the respective stock solutions. The p_H of the solutions varied between 5.75 and 5.80. So the hydrogen-ion concentration of the solutions in both the half elements was nearly the same. Thus the junction potential was eliminated to a large extent.

The mercury/mercurous acetate cells were set up in the same way as in our previous work (this *Journal*, 1952, **29**, 169). The bridge solution was saturated potassium chloride. All the measurements were done at 35° and in duplicate which agreed within 0.2 mv. The experimental results are recorded in Table I.

TABLE I

$Hg, Hg_2Ac_2 \mid NaAc\,(m') \parallel$ satd. KCl bridge $\parallel NaAc\,(m') \; Co(NO_3)_2\,(m) \mid Hg_2Ac_2, Hg$

Concentration of sodium acetate.	Concentration of cobalt nitrate.	E.M.F. in (volts)	Mean E.M.F. (volts)	Activity of Ac^- ion.	Degree of dissn. (β)	Ionic strength.	$K \times 10^2$.
0.01 *M*	0.0260 *M*	0.0052	0.0052	0.0074	0.950	—	—
0.02	0.0260	0.0074 0.0071	0.0073	0.0132	0.851	0.092	*5.20
0.02	0.0104	0.0037 0.0033	0.0035	0.0153	0.870	0.048	5.75
0.04	0.0260	0.0065 0.0067	0.0066	0.0261	0.771	0.016	4.40
0.04	0.0521	0.0106 0.0106	0.0010	0.0234	0.809	0.181	*6.10
0.06	0.0521	0.0095 0.0095	0.0095	0.0339	0.746	0.189	4.40
0.06	0.0781	0.0012 0.0126	0.0126	0.0301	0.719	0.260	4.50
0.08	0.0520	0.0094 0.0090	0.0092	0.0446	0.669	0.201	3.99
0.08	0.1041	0.0140 0.0145	0.0143	0.0369	0.679	0.341	4.55
0.10	0.1041	0.0135 0.0138	0.0136	0.0461	0.679	0.348	4.17
0.10	0.1560	0.0178 0.0182	0.0180	0.0391	0.595	0.487	4.50

Mean value of K (excluding those with asterisk marks) = 4.35×10^{-2}.

The E.M.F. of the cells of the type,

$$Hg, Hg_2Ac_2 \mid NaAc(m') \parallel \begin{matrix} NaAc(m') \\ Co(NO_3)_2(m) \end{matrix} \mid Hg_2Ac_2, Hg,$$

can be had from the equation

$$E = 2.303 \frac{RT}{F} \log_{10} \frac{a'_{Ac^-}}{a''_{Ac^-}}$$

where a'_{Ac^-} and a''_{Ac^-} are the activities in NaAc and NaAc+CO $(NO_3)_2$ solutions respectively, if we assume that the junction potential has been eliminated by the use of salt bridge or is negligible. Since sodium acetate dissociates completely,

$$E = 2.303 \log_{10} \frac{m' f_{Ac^-}}{a''_{Ac^-}}$$

where m' and f_{Ac^-} are the concentration and activity coefficient of the acetate ion in sodium acetate solution. The activity coefficient of the acetate ion was taken to be equal to that of Cl^- ion in solution having the same ionic strength. So substituting the

values of m and f_{Ac^-} in the above equation, the values of a''_{Ac^-} in the other solution containing both sodium acetate and cobalt nitrate was calculated. They are shown in column 5.

Now let us assume that there is interaction between Co^{2+} and Ac^- ions to give $CoAc^+$, or in other words, cobalt acetate dissociates according to the scheme,

$$CoAc_2 \xrightarrow{\text{complete}} CoAc^+ + Ac^-$$
$$\Updownarrow$$
$$Co^{2+} + Ac^-$$

In the solution containing sodium acetate and cobalt nitrate, the concentration of these salts is not always equimolecular.

Let us consider the case when molal concentration of cobalt nitrate (m) is greater than that of sodium acetate (m'). Then

$$[Na^+] = m' \text{ and } [NO_3^-] = 2m,$$
$$[CoAc^+] = (1-\beta)\,m',\ [Ac^-] = \beta m', \text{ where } \beta \text{ is the degree of dissociation of } CoAc^+.$$
$$[Co^{2+}] = [Co^{2+}]_1 + [Co^{2+}]_2$$

from excess of cobalt nitrate and from dissociation of $CoAc^+$ respectivly Therefore the ionic strength of the solution is $3m - m' + 2\beta m'$ to evaluate which a knowledge of β is necessary. That has been done by an approximation method. At first it has been assumed that $CoAc^+$ is undissociated. Then the ionic strength will be given by the expression $\mu = 3m - m'$. For this ionic strength the activity coefficient of acetate ion has been found, and a value of β obtained from the relationship

$$\beta = \frac{a_{Ac^-}}{m' f_{Ac^-}}.$$

A more accurate value of the ionic strength is then found using the equation

$$\mu = 3m - m' + 2\beta m'.$$

Putting the value of activity coefficient for this new ionic strength, a more accurate value of β is obtained. This process of approximation is repeated till β assumes a constant value. Thus the degree of dissociation has been calculated for each concentration. In column 6 are shown the values of β and in column 7, the respective ionic strength.

Another case may arise when molal concentration of sodium acetate is greater than the concentration of cobalt nitrate, i. e. $m' > m$.

Let $[NaAc] = m'$; $[Co(NO_3)_2] = m$
$[Na^+] = m'$; $[NO_3^-] = 2m$
$[CoAc^+] = (1-\beta)m$; $[Ac^-] = m' - m + \beta m$; $(Co^{2+}) = \beta m$.

The ionic strength of the solution is given by the equation,

$$\mu = m + m' + 2\beta m.$$

Here also using the method of approximation the values of degree of dissociation for different concentrations have been calculated. They are given in column 8 of the table.

The values of β show that complete dissociation of the first stage is justified. Even the dissociation of $CoAc^+$ is quite high at lower concentrations. At 0.01M, it is about 0.95, so that the evaluation of the equilibrium constant becomes impossible in view of the limitation of accuracy of the experimental technique. So for the purpose of calculations, measurements for concentration of 0.02M and higher have been used. The expression for the constant for the equilibrium,

$$CoAc^+ \rightleftarrows Co^{2+} + Ac^-$$

is given by the equation,

$$K = \frac{[Co^{2+}]\,[Ac^-]}{[CoAc^+]} = \frac{[Co^{2+}]\,[Ac^-]\,f_{Co^{2+}}\,f_{Ac^-}}{[CoAc^+]\,f_{CoAc^+}} = \frac{[Co^{2+}]\,[Ac^-]\,f_{Co^{2+}}}{[CoAc^+]},$$

assuming $f_{CoAc^+} = f_{Ac^-}$

Column 8, gives the values of K calculated on the basis of the above equation, assuming the activity coefficient of Co^{2+} to be equal to that of Ba^{2+} ion in solution having the same ionic strength. The values of K are fairly constant. The constancy of K also justifies our assumption about the complete dissociation of $CoAc_2$ into $CoAc^+$ and Ac^-, for if it were not so, some deviation would have been found at least in cases where the amount of sodium acetate is greater. The mean value of K calculated from those given in column 8 of the table excluding those with asterisk mark comes out to be 4.35×10^{-2}.

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m-ALKYLPHENOLS

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RMgX (R=normal C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17} and $C_{12}H_{25}$) has been condensed with *m*-methoxybenzamide and the resulting *m*-methoxyphenylalkyl ketones have been demethylated and reduced to the corresponding *m*-alkylphenols.

With a view to studying their physicochemical and pharmacological properties, *m*-alkylphenols have been prepared in this laboratory.

Organo-magnesium compounds react with acid amides to furnish ketones. Beise (*Compt. rend.*, 1903, **137**, 375) obtained aliphatic ketones in yields of 20 to 50% by this method. Using the procedure of Jenkins and Richards (*J. Amer. Chem. Soc.*, 1933, **55**, 703, 1618, 2896) alkylmagnesium halides (from normal butyl, amyl, hexyl, heptyl, octyl and lauryl halides) have been condensed with *m*-methoxybenzamide, and *m*-methoxyphenylalkyl ketones obtained in 60-70% yield. These ketones on demethylation by anhydrous aluminium chloride gave *m*-hydroxyphenylalkyl ketones which on modified Clemmensen reduction (Brady and Day, *J. Chem. Soc.*, 1934, 117) yielded *m*-alkylphenols. *m*-Alkylphenols were characterised by the preparation of phthalimido-N-methylene ether derivatives (Mancera and Lamberger, *J. Org. Chem.*, 1950, **15**, 1253).

Experimental

Condensation of the Grignard Reagents from Alkyl Halides with m-*Methoxybenzamide.*—To a Grignard reagent, prepared from magnesium turnings (0.3 *M*), *n*-alkyl bromide (0.3 *M*), and dry ether (200 c.c.), was added thoroughly dried and powdered *m*-methoxybenzamide (0.1 *M*) in small lots. The reaction was carried out at 60° and under hydrogen atmosphere. After heating the reaction mixture for 48 hours it was decomposed with ice and dilute sulphuric acid (100 c.c., 25%) and the ketone was recovered as usual.

Demethylation of m-*Methoxyphenyl*-n-*alkyl Ketones.*—A mixture of *m*-methoxyphenyl-*n*-alkyl ketone (0.1 *M*), benzene (100 c.c.) and anhydrous aluminium chloride (28 g.) was heated on a water-bath for 2 hours. The reaction mass was decomposed with ice and HCl and the benzene layer was extracted with NaOH solution (2%). The alkali extract on acidification gave *m*-hydroxyphenyl-*n*-alkyl ketone, yield 80%.

Reduction of m-*Hydroxyphenyl*-n-*Alkyl Ketones.*—To a refluxing mixture of amalgamated zinc (15 g.), HCl (dilute, 30 c.c., 1 : 1) and ethyl alcohol (15 c.c.) was added *m*-hydroxyphenyl-*n*-alkyl ketone (4 g.) in three lots, followed by HCl (dilute, 10 c.c., 1 : 1) at intervals of half an hour. Heating was continued for 20 hours with addition of HCl (10 c.c., 1 : 1) every three hours. The resulting *m*-alkylphenols were recovered as usual. The compounds prepared are shown in the table.

TABLE I

Name of the compound.	Formula.	Properties.	M.P. or B.P.	Analysis. Found.	Calc.
m-Methoxyphenyl-*n*-butyl ketone	$C_{12}H_{16}O_2$	Colourless liquid; d^{30}_4, 1.012; $n_D^{31\cdot5}$, 1.5242	190°/30 mm.	C : 75.2% H : 8.3	75.0% 8.4
Semicarbazone of above	$C_{13}H_{19}O_2N_3$	Needles from alcohol	138°	N : 17.0	16.9
2 : 4-Dinitrophenylhydrazone of above	$C_{18}H_{20}O_5N_4$	Orange plates from alcohol	147°	N : 14.8	15.0
m-Hydroxyphenyl-*n*-butyl ketone	$C_{11}H_{14}O_2$	Plates from dil. alcohol	67°	C : 74.4 H : 7.8	74.2 7.9
p-Nitrophenylhydrazone of above	$C_{17}H_{19}O_3N_3$	Orange plates from alcohol	111°	N : 13.6	13.4
m-*n*-valeroylphenoxyacetic acid	$C_{13}H_{16}O_4$	Needles from water	70°	C : 66.0 H : 6.6 Equiv. 236.2	66.1 6.8 236.0
m-*n*-Amylphenol	$C_{11}H_{16}O$	Colourless liquid; n^{35}_D, 1.533	135°/10 mm.	C : 80.3 H : 9.6	80.4 9.8
N-Phthalimidomethylene ether of above	$C_{20}H_{21}O_3N$	Plates from petrol ether	123°	N : 4.4	4.3
m-Methoxyphenyl-*n*-amyl ketone	$C_{13}H_{18}O_2$	Colourless liquid; d^{29}_4, 0.9980; n^{35}_D, 1.5189	220°/20 mm.	C : 75.5 H : 8.5	75.7 8.7
Semicarbazone of above	$C_{14}H_{21}O_2N_3$	Needles from alcohol	108°	N : 16.1	16.0
2 : 4-Dinirtophenylhydrazone of above	$C_{19}H_{22}O_5N_4$	Orange plates from alcohol	148°	N : 14.6	14.5
m-Hydroxyphenyl-*n*-amyl ketone	$C_{12}H_{16}O_2$	Plates from petrol ether	63°	C : 74.7 H : 8.4	75.0 8.3
Semicarbazone of above	$C_{13}H_{19}O_2N_3$	Needles from alcohol	101°	N : 17.0	16.9
p-Nitrophenylhydrazone of above	$C_{18}H_{21}O_3N_3$	Yellow needles from alcohol	158°	N : 12.8	12.9
m-Caproylphenoxyacetic acid	$C_{14}H_{18}O_4$	Needles from water	71°	C : 67.0 H : 7.1 Equiv. 248.5	67.2 7.2 250.0
m-*n*-Hexylphenol	$C_{12}H_{18}O$	Colourless liquid; n^{31}_D; 1.5155	150°/10 mm.	C : 80.7 H : 10.0	80.9 10.1
N-Phthalimidomethylene ether of above	$C_{21}H_{23}O_3N$	Plates from petrol ether	126°	N : 4.2	4.1
m-Methoxyphenyl-*n*-hexyl ketone	$C_{14}H_{20}O_2$	Colourless liquid; d^{28}_4, 1.034; n^{35}_D, 1.5171	235°/20 mm.	C : 76.1 H : 8.9	76.4 9.1
Semicarbazone of above	$C_{15}H_{23}O_2N_3$	Needles from alcohol	121°	N : 15.3	15.2
2: 4-Dinitrophenylhydrazone of above	$C_{20}H_{24}O_5N_4$	Orange plates from alcohol	107°	N : 14.2	14.0
m-Hydroxyphenyl-*n*-hexyl ketone	$C_{13}H_{18}O_2$	Needles from petrol, ether or dilute alcohol.	62°	C: 75.8 H : 8.6	75.7 8.7
Semicarbazone of above	$C_{14}H_{21}O_2N_3$	Needles from alcohol	121°	N : 15.9	16.0
p-Nitrophenylhydrazone of above	$C_{19}H_{23}O_3N_3$	Yellow needles from alcohol	143°	N : 12.2	12.3

TABLE I (contd.)

Name of the compound.	Formula.	Properties.	M.P. or B.P.	% Analysis. Found.	Calc.
m-*n*-Heptoylphenoxyacetic acid	$C_{15}H_{20}O_4$	Needles from water	65°	C : 68.0 H : 7.4 Equiv. 263	68.2 7.6 264
m-*n*-Heptylphenol	$C_{13}H_{20}O$	Colourless liquid; n^{36}_D, 1.517	175°/15mm.	C : 81.1 H : 10.3	81.2 10.4
N-Phthalimidomethylene ether of above	$C_{22}H_{23}O_3N$	Plates from petrol ether	131°	N : 4.0	4.0
m-Methoxyphenyl-*n*-heptyl ketone	$C_{15}H_{22}O_2$	Colourless liquid; n_D, $^{31.5}$ 1.4700	160°/15	C : 76.7 H : 9.3	76.9 9.4
Semicarbazone of above	$C_{16}H_{25}O_2N_3$	Needles from alcohol	72°	N : 14.5	14.4
2:4-Dinitrophenylhydrazone of above	$C_{21}H_{26}O_5N_4$	Orange plates from alcohol	90°	N : 13.6	13.5
m-Hydroxyphenyl-*n*-heptyl ketone	$C_{14}H_{20}O_2$	Plates from dilute alcohol	58°	C : 76.4 H : 9.2	76.3 9.1
Semicarbazone of above	$C_{15}H_{23}O_2N_3$	Needles from alcohol	94°	N : 15.0	15.1
p-Nitrophenylhydrazone of above	$C_{20}H_{25}O_3N_3$	Orange plates from alcohol	113°	N: 11.9	11.8
m-*n* Caprylylphenoxyacetic acid	$C_{16}H_{22}O_4$	Needles from water	69°	C : 69.2 H : 7.8 Equiv. 276.8	69.1 7.9 278.0
m-*n* Octylphenol	$C_{14}H_{22}O$	Colourless liquid; n^{35}_D, 1.5175	110°/10 mm.	C : 81.4 H : 10.6	81.5 10.7
N-Phthalimidomethylene ether of avobe	$C_{23}H_{27}O_3N$	Needles from petrol ether	133°	N : 3.7	3.8
m-Methoxyphenyl-*n*-octyl ketone	$C_{16}H_{24}O_2$	Colourless liquid; d_4^{29}, 0.9570 ; n^{37}_D, 1.507	170°/14 mm.	C : 77.3 H : 9.5	77.4 9.7
Semicarbazone of above	$C_{17}H_{27}O_2N_3$	Needles from alcohol	84°	N : 13.9	13.8
2:4-Dinitrophenylhydrazone of above	$C_{22}H_{28}O_5N_4$	Orange plates from alcohol	90°	N : 13.3	13.1
m-Hydroxyphenyl-*n*-octyl ketone	$C_{15}H_{22}O_2$	Plates from dilute alcohol	54°	C : 76.7 H : 9.7	76.9 9.5
Semicarbazone of above	$C_{16}H_{25}O_2N_3$	Plates from alcohol	112°	N : 14.6	14.4
p-Nitrophenylhydrazone of above	$C_{21}H_{27}O_3N_3$	Yellow plates from alcohol	101°	N : 11.5	11.4
m-*n*-Pelargonylphenoxy-acetic acid	$C_{17}H_{24}O_4$	Needles from water	60°	C : 70.0 H : 8.2 Equiv. 290.7	69.9 8.2 292
m-*n*-Nonylphenol	$C_{15}H_{24}O$	Colorless liquid; n^{39}_D, 1.575	155°/25	C : 81.7 H : 10.7	81.8 10.9
N-Phthalimidomethylene ether of above	$C_{24}H_{29}O_3N$	Needles from petrol ether	144°	N : 3.8	3.7

TABLE I (contd.)

Name of the compound.	Formula.	Properties.	M.P. or B.P.	% Analysis. Found.	Calc.
m-Methoxyphenyl-*n*-lauryl ketone	$C_{20}H_{32}O_2$	Colorless liquid; n^{37}_D, 1.4405	210°/25	C : 78.8 H : 10.4	78.9 10.5
Semicarbazone of above	$C_{21}H_{35}O_2N_3$	Needles from alcohol	59°	N : 11.5	11.6
2 : 4-Dinitrophenylhydrazone of above	$C_{26}H_{36}O_5N_4$	Orange plates from alcohol	79°	N : 11.5	11.6
m-Hydroxyphenyl-*n*-lauryl ketone	$C_{19}H_{30}O_2$	Colorless liquid, n^{36}_D, 1.556	165°/25 mm.	C : 78.8 H : 10.4	78.6 10.5
2 : 4-Dinitrophenylhydrazone of above	$C_{25}H_{34}O_5N_4$	Orange plates from alcohol	100°	N : 12.0	11.9
m-*n*-Tridecylphenol	$C_{19}H_{32}O$	Colorless liquid; n^{36}_D, 1.5302	160°/15 mm.	C : 82.6 H : 11.7	82.6 11.6
N-phthalimidomethylene ether of above	$C_{28}H_{37}O_3N$	Plates from petrol ether	124°	N : 3.2	3.2

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FRIEDEL AND CRAFT'S ACYLATION OF ETHYL *p*-HYDROXYBENZOATE

By M. P. Fadia, V. P. Shukla and J. J. Trivedi

4-Hydroxy-3-acylbenzoic acids have been obtained by condensing acyl chlorides with ethyl *p*-hydroxybenzoate in presence of anhydrous aluminium chloride in acetylene tetrachloride as a solvent.

Carboxyl (or carbethoxy) group has an inhibiting effect on Friedel and Craft's acylation of aromatic compounds (Kunckell, *Ber.*, 1905, **38,** 2609). Limpricht (*Annalen*, 1896, **290,** 164; 1898, **303,** 274) failed to condense acyl chlorides with ethyl *p*-hydroxybenzoate in presence of anhydrous aluminium chloride. Acetylene tetrachloride has been successfully used as a solvent for the succinoylation of phenols and cresols (Raval, Bokil and Nargund, *J. Univ. Bombay*, 1938, **7,** 184). Using acetylene tetrachloride as a solvent acyl chlorides have now been condensed with ethyl *p*-hydroxybenzoate to yield 4-hydroxy-3-acylbenzoic acids in 70-80% yields.

Experimental

Condensation of Acyl Chlorides with Ethyl p-*Hydroxybenzoate.*—To a mixture of ethyl *p*-hydroxybenzoate (0.1 *M*), acyl chloride (0.1 *M*) and freshly distilled acetylene tetrachloride (150 c.c.) was added powdered anhydrous aluminium chloride (28 g.) in small lots with occasional agitation. The reaction mixture was then heated in an oil-bath at 120° for 3 to 4 hours. The semisolid reaction mass was cooled, decomposed with ice and HCl (conc., 150 c.c.) and the solvent removed by steam distillation. The residue was digested with hot sodium carbonate solution (animal charcoal), filtered and the 4-hydroxy-3-acylbenzoic acids were liberated from the filtrate by HCl. The compounds prepared are shown in the table.

Table I

Name of the compound.	Formula.	Properties.	M.P. or B.P.	%Analysis. Found.	Calc.
*4-Hydroxy-3-acetylbenzoic acid	$C_9H_8O_4$	Needles from alcohol	241°	C : 59.8 H : 4.4 Equiv. 176.6	60.0 4.5 180.0
*Semicarbazone of above	$C_{10}H_{11}O_4N_3$	Do	290°	Equiv. 236.2	237.0
*Oxime of above	$C_9H_9O_4N$	Prismatic needles	255°	N : 7.1	7.2
4-Hydroxy-3-propionylbenzoic acid	$C_{10}H_{10}O_4$	Needles from alcohol	220°	C : 61.7 H : 5.0 Equiv. 193.6	61.9 51.2, 194.0
Semicarbazone of above	$C_{11}H_{13}O_4N_3$	Do	298°	Equiv. 250.9	251.0
Oxime of above	$C_{10}H_{11}O_4N$	Prismatic needles	212°	N : 6.8	6.7
Ethyl ester of above	$C_{12}H_{14}O_4$	Needles from dilute alcohol	65°	C : 64.8 H : 6.2	64.9 6.3
4-Acetoxy-3-propionylbenzoic acid	$C_{12}H_{12}O_5$	Needles from dilute acetic acid	160°	Equiv. 233.3	236.0
4-Methoxy-3-propionylbenzoic acid	$C_{11}H_{12}O_4$	Needles from alcohol	194°	,, 206.0	208.0

TABLE I (contd.)

Name of the compound.	Formula.	Properties.	M.P. or B.P.	%Analysis. Found.	Calc.
4-Hydroxy-3-butyrylbenzoic acid	$C_{11}H_{12}O_4$	Needles from alcohol	202°	C : 63.4 H : 5.6 Equiv. 205.4	63.5 5.8 208.0
Semicarbazone of above	$C_{12}H_{15}O_4N_3$	Do	292°	Equiv. 263.5	265.0
Oxime of above	$C_{11}H_{13}O_4N$	White plates	199°	N : 6.2	6.3
Ethyl ester of above	$C_{13}H_{16}O_4$	Colourless liquid ; n^{34}_D, 1.5268	180°/35 mm	C : 66.0 H : 6.8	66.1 6.8
4-Acetoxy-3-butyrylbenzoic acid	$C_{13}H_{14}O_5$	Plates from dilute acetic acid	113°	Equiv. 246.1	250.0
4-Methoxy-3-butyrylbenzoic acid	$C_{12}H_{14}O_4$	Needles from alcohol	185°	„ 219.1	222.0
4-Hydroxy-3-valerylbenzoic acid	$C_{12}H_{14}O_4$	Plates from alcohol	184°	C : 64.7 H : 6.2 Equiv. 216.4	64.9 6.3 222.0
Semicarbazone of above	$C_{13}H_{17}O_4N_3$	Needles from alcohol	292°	Equiv. 281.3	279.0
Oxime of above	$C_{12}H_{15}O_4N$	Prismatic needles	183°	N : 6.0	5.9
Ethyl ester of above	$C_{14}H_{18}O_4$	Colorless liquid ; n^{34}_D, 1.5220 ; d^{28}_4, 1.1080	190°/30 mm.	C : 67.3 H : 7.0	67.2 7.2
4-Acetoxy-3-valerylbenzoic acid	$C_{14}H_{16}O_5$	Plates from dilute acetic acid	101°	Equiv. 261.0	264·0
4-Methoxy-3-valerylbenzoic acid	$C_{13}H_{16}O_4$	Needles from alcohol	154°	„ 235.0	236.0
4-Hydroxy-3-caproylbenzoic acid	$C_{13}H_{16}O_4$	Plates from alcohol	188°	C : 66.0 H : 6.7 Equiv. 238.0	66.1 6.8 236.0
Semicarbazone of above	$C_{14}H_{19}O_4N_3$	Needles from alcohol	290°	Equiv. 289.1	293.0
Oxime of above	$C_{13}H_{17}O_4N$	Prismatic needles	218°	N : 5.7	5.6
Ethyl ester of above	$C_{15}H_{20}O_4$	Colorless liquid ; $n^{35\cdot5}_D$, 1.5280	200°/20mm.	C : 68.2 H : 7.5	68.2 7.6
4-Acetoxy-3-caproylbenzoic acid	$C_{15}H_{18}O_5$	Needles from dilute acetic acid	100°	Equiv. 280.5	278.0
4-Methoxy-3-caproylbenzoic acid	$C_{14}H_{18}O_4$	Needles from alcohol	160°	„ 245.0	250.0
4-Hydroxy-3-heptoylbenzoic acid	$C_{14}H_{18}O_4$	Plates from alcohol	183°	C : 67.0 H : 7.3 Equiv. 252.0	67.2 7.2 250.0
Semicarbazone of above	$C_{15}H_{21}O_4N_3$	Needles Do	224°	Equiv. 310.0	307.0
Oxime of above	$C_{14}H_{19}O_4N$	Prismatic needles	171°	N : 5.1	5.3
Ethyl ester of above	$C_{16}H_{22}O_4$	Colorless liquid ; $n^{35\cdot5}_D$, 1.5115	210°/22mm.	C : 69.2 H : 8.1	69.0 7.9

TABLE I (contd.)

Name of the compound.	Formula.	Properties.	M.P. or B.P.	%Analysis	
				Found.	Calc.
4-Acetoxy-3-heptoylbenzoic acid	$C_{16}H_{20}O_5$	Plates from dilute acetic acid	101°	Equiv. 290.0	292.0
4-Methoxy-3-heptoylbenzoic acid	$C_{15}H_{20}O_4$	Plates from alcohol	163°	Equiv. 262.0	264.0
4-Hydroxy-3-benzoylbenzoic acid	$C_{14}H_{10}O_4$	Plates from alcohol	265°	C : 69.3 H : 4.0 Equiv. 240.0	69.4 4.1 242.0
Semicarbazone of above	$C_{15}H_{13}O_4N_3$	Needles from alcohol	300°	Equiv. 296.0	299.0
Ethyl ester of above	$C_{16}H_{14}O_4$	Plates from alcohol	104°	C : 71.0 H : 51	171.1, H : 5.2

* Shah and Shah (this *Journal*, 1949, **26**, 235) give the m.p. as 241°, 290° and 259°-60° for the acid (obtained by the Fries migration of ethyl-4-acetoxybenzoate), semicarbazone and the oxime respectively.

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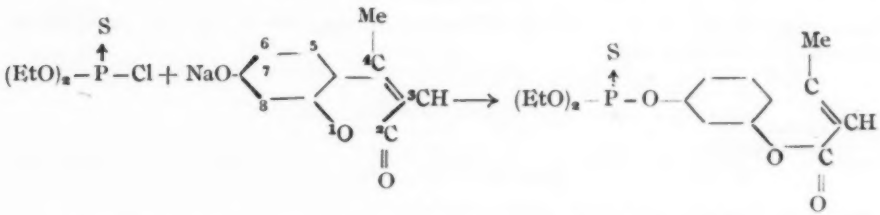
SEARCH FOR NEW INSECTICIDES. PART IX

By A. B. Sen and A. K. Sen Gupta

o:*o*-Diethyl chlorothiophosphate has been condensed with several 7-hydroxycoumarins to yield compounds of the type of Parathion; they have been further condensed with ethyl chlorohydrin and phosphorus oxychloride to obtain the corresponding ethers and phosphoric esters which are expected to possess insecticidal activity.

The insecticidal activity of rotenone and pyrethrin is ascribed to the presence of carbonyl groups which act as toxophores. Such a group is present in coumarins and chromones. Organo-phosphorus compounds are known to possess powerful insecticidal properties, their activity in this respect being enhanced by the presence of acidic substituents or acid anhydride residues in the molecule. 7-Hydroxycoumarins were therefore condensed with *o* : *o*-diethyl chlorothiophosphate (Fletcher *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3943).



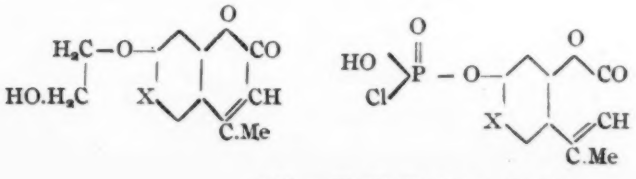
For useful systemic action, the insecticide should be soluble in plant sap. 7-Hydroxy-6-alkylcoumarins were therefore condensed with ethylene chlorohydrin as the products so obtained contained hydroxyethyl group on one side and an alkyl group on the other.

Maguire and Shaw (*J. Chem. Soc.*, 1953, 1479) observe that the esters of phosphoric acid are also effective in controlling the growth of plants with long tap roots. Hence, such esters have been prepared from the 7-hydroxycoumarins and phosphorus oxychloride.

The sodium salts of hydroxycoumarins (Pechmann, *Ber.*, 1884, **17**, 929), hydroxyalkyl- and chloro-coumarins (Knoevenagel, *Ber.*, 1898, **31**, 2585; cf. Chakravarti, this *Journal*, 1939, **16**, 144) were refluxed with *o* : *o*-diethyl chlorothiophosphate (1 mole) for one hour and the respective products isolated according to Fletcher *et al.* (*loc. cit.*).

Similarly, the coumarins were condensed with ethylene-chlorohydrin in an inert solvent. The product separated out when the reacting mixture was poured into water.

The phosphoric acid esters were obtained by refluxing the coumarin (1 mole) with phosphorus oxychloride (3 moles) in an inert solvent in the presence of magnesium turnings (0.1 g.). The product obtained by pouring the reacting mixture into water was crystallised from a suitable solvent (Maguire and Shaw, *loc. cit.*).



[X = H, Cl, Et, Pr or Bu]

Experimental

The alkylresorcinols required for this investigation were obtained by the Clemmensen reduction of the corresponding acylresorcinols, prepared according to Hoesch (*Ber.*, 1915, **48,** 1122) and Johnson and Lane (*J. Amer. Chem. Soc.*, 1921, **43,** 357) respectively.

4-Chlororesorcinol was obtained by the action of sulphuryl chloride on resorcinol (Reinhardt, *J. prakt. Chem.*, 1878, *ii*, **17,** 322 ; cf. Chakravarti, *loc. cit.*).

Thiophosphoryl chloride was prepared by heating phosphorus pentasulphide (1 mole) and phosphorus pentachloride (3 moles) in a sealed tube at 120° for about 2 hours. Thiophosphoryl chloride distilled over at 125°/760mm., yield 90% (Newton Friend, "Text Book of Inorganic Chemistry," Vol. I).

o : o-*Diethyl Chlorothiophosphate.*—Thiophosphoryl chloride (20 g.) in 50 c.c. benzene was added to a stirred solution of sodium ethoxide (from 5.5 g. of sodium in 75 c.c. of ethanol), the reaction temperature being held at 5°-10° (Fletcher *et al.*, *loc. cit.*). *o* : *o*-Diethyl chlorothiophosphate distilled at 80°/10 mm., yield 50%.

7-O-(o : o-*Diethylthiophosphoryl*)-*coumarin.*—A mixture of *o* : *o*-diethyl chlorothiophosphate (1 mole), anhydrous sodium salt of the hydroxycoumarin (1 mole) and ethanol was refluxed for one hour, cooled to 20°, filtered and the filtrate concentrated in vacuum. The residue was heated for a short period to remove any unchanged *o* : *o*-diethyl chlorothiophosphate. The crude product was dissolved in toluene and washed with 5% sodium carbonate, then with water. After drying over anhydrous sodium sulphate, toluene was removed under reduced pressure and the product was distilled. The boiling points, yield and analytical data are recorded below.

Table I

	B.P.	Yield.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
7-O-(*o*: *o*-diethylthiophosphoryl)-coumarin	170°/8mm.	55%	44.9	45.0	4.1	4.3
-4-methyl-6-chloro-	165°/10	56	42.0	42.5	4.02	4.05
-4-methyl-6-ethyl-	112°/10	65	48.9	49.4	5.2	5.4
-4-methyl-6-propyl-	145°/8	55	50.1	50.7	5.4	5.7
-4-methyl-6-butyl-	135°/8	56	51.2	51.9	5.9	6.0

7-O-(*β-Hydroxyethyl*)-*coumarin.*—Sodium derivatives of coumarins were first prepared from sodium (1 mole) and coumarin (1 mole) in an inert solvent like benzene or dioxane. Equivalent amount of ethylene-chlorohydrin was added dropwise. After completion of the reaction the mixture was poured in water and the ether separating was crystallised from alcohol. The melting points, yield and analytical data are recorded below.

TABLE II

	M.P.	Yield.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
7-O-(β-Hydroxyethyl)-coumarin	225°	65%	63.8	64.0	4.5	4.8
-4-methyl-6-chloro-	200°	66	65.0	65.7	4.9	5.0
-4-methyl-6-ethyl-	208°	50	67.8	68.0	6.0	6.07
-4-methyl-6-propyl-	175°	80	67.9	68.6	6.1	6.8
-4-methyl-6-butyl-	100°	65	68.9	69.0	6.1	6.9

7-O-(*Chlorophosphoryl*)-*coumarin*.—Hydroxycoumarin (1 mole) in an inert solvent (benzene or dioxane), $POCl_3$ (3 moles) and magnesium turnings (0.1 g.) were boiled for 3 hours, HCl being steadily evolved. After completion of the reaction it was added to water under stirring. Chlorophosphorylcoumarin when separated out was recrystallised from alcohol (Maguire and Shaw, *loc. cit.*). The melting points, yield and the analysis are recorded below.

TABLE III

	M.P.	Yield.	% Carbon Found.	% Carbon Calc.	% Hydrogen Found,	% Hydrogen Calc.
7-O-(Chlorophosphoryl)-coumarin	198°	90%	40.9	41.3	2.0	2.3
-4-methyl-6-chloro-	230°	80	38.0	38.7	2.1	2.5
-4-methyl-6-ethyl-	160°	80	47.1	47.5	3.1	3.9
-4-methyl-6-propyl-	149°	75	48.9	49.1	4.0	4.4
-4-methyl-6-butyl-	157°	60	49.7	50.7	4.1	4.8

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STUDIES ON THE VELOCITY OF FLOW OF SOLVENTS THROUGH CHROMATOGRAPHIC COLUMNS. PART III. RELATION BETWEEN VOLUME OF FLOW OF THE SOLVENT PER UNIT TIME AND THE HEIGHT OF THE ADSORBENT COLUMNS

By D. R. Gupta and Abani K. Bhattacharya

The volume of flow per unit time per unit height of the column (Vh/t) has been determined for water, methyl alcohol, methyl acetate, acetone and benzene through calcium carbonate, silicic acid, Fuller's earth, Kieselguhr and magnesium oxide columns. Vh/t gives a constant value after an optimum height has been reached. Below this height, the values of Vh/t are slightly lower and approach constancy as the height of the column is increased.

In continuation of our previous communication (Part II, this *Journal*, 1954, **31**, 431) it was considered necessary to investigate further if the value of Vh/t remained constant for all heights of the adsorbent column. With this object in view, the velocity of flow, measured in terms of volume per unit time, was determined for different heights of $CaCO_3$, silicic acid, Fuller's earth, Kieselguhr and MgO in the chromatographic tube and the values of Vh/t were determined for the typical solvents like water, methyl alcohol, methyl acetate, acetone and benzene.

Experimental

The adsorbent was very finely powdered, passed through a standard sieve in every case and then stirred thoroughly in the solvent and warmed to expel the dissolved air, if any. The chromatographic tube having a bed of asbestos wool of constant thickness over the porcelain sieve at the bottom was uniformly packed as far as possible, by manipulation, as described in Part I (*ibid.*, 1953, **30**, 666). The solvent was made to flow under a constant suction force by the same arrangement as explained in Part II (*loc. cit.*) and the rate of flow per unit time was determined for different values of h. The values of Vh/t, defined as the volume of the solvent flown per unit time (t) per unit height (h) of the adsorbent column, were then calculated. The observations made are recorded in the following tables.

Table I

Height of the Hg in the manometer = 34.5 cm. Temperature = 21.5° ± 1. Volume of solvent (V) = 2c.c. Absorbent: $CaCO_3$.

Water.

Solvent.									
	Height (cm.)	1.50	2.12	3.21	4.26	5.40	6.18	7.25	8.0 cm.
Water (V=2c.c.)	Vh/t	0.0175	0.0182	0.0197	0.0210	0.0222	0.0223	0.0223	0.0223

MeOH.

MeOH (V=2c.c.)								
Height (cm.)	1.70	2.89	3.95	4.61	5.24	6.63	7.45	
Vh/t	0.0185	0.0196	0.0197	0.0201	0.0207	0.0207	0.0207	

MeAc.

MeAc (V=2c.c.)							
Height (cm.)	1.42	2.34	3.21	4.10	5.43	6.29	7.45
Vh/t	0.0362	0.0434	0.0485	0.0514	0.0520	0.0520	0.0520

Acetone.

Acetone(V=5c.c.)							
Height (cm.)	1.63	2.97	3.64	4.25	5.16	6.25	7.14
Vh/t	0.0890	0.0914	0.0958	0.101	0.101	0.101	0.101

Benzene.

Benzene (V=2c.c.)							
Height (cm.)	1.23	2.32	3.56	4.67	5.37	6.29	7.43
Vh/t	0.145	0.167	0.180	0.187	0.187	0.187	0.188

TABLE II

Adsorbent : silicic acid.

	Height. (cm.)	1.15	2.39	3.51	4.40	5.85	6.45	7.56
Water (V=2.5 c.c.)	Vh/t	0.0271 (V=5 c.c)	0.0371	0.0391	0.0403	0.0407	0.0408	0.0408
MeOH (V=2 c.c.)	Height	1.46	2.61	3.48	4.50	5.32	6.64	7.25
	Vh/t	0.0304	0.0315	0.0323	0.0325	0.0331	0.0339	0.0339
MeAc (V=2 c.c.)	Height	1.73	2.93	4.17	4.50	5.59	6.42	
	Vh/t	0.0964	0.0999	0.102	0.105 (V=4c.c)	0.105 (V=4c.c.)	0.105 (V=4c.c.)	
Acetone (V=5 c.c.)	Height	1.25	2.56	3.45	4.50	5.65	6.28	
	Vh/t	0.0957	0.0980	0.100	0.105	0.1045	0.1048	
Benzene (V=2 c.c.)	Height	1.48	2.25	3.80	4.50	5.25	6.30	
	Vh/t	0.0832	0.0922	0.110	0.115	0.115	0.115	

TABLE III

Adsorbent : Fuller's earth.

	Height (cm.)	1.46	2.47	3.13	4.28	5.78	6.80	
Water (V=1 c.c.)	Vh/t	0.0052	0.0062	0.0063	0.0076	0.0076	0.0076	
MeOH (V=1 c.c.)	Height	1.26	2.21	3.03	4.50	5.35	6.24	7.60
	Vh/t	0.0168	0.0184	0.0194	0.0214	0.0224	0.0226	0.226
MeAc (V=4 c.c.)	Height	1.55	2.22	3.39	4.50	5.19	6.33	7.25
	Vh/t	0.969	0.108	0.109	0.110	0.111	0.111	0.111
Acteone (V=5,4,4,2, 2,2,2 resptly)	Height	1.64	2.88	3.70	4.50	5.19	6.10	7.25
	Vh/t	0.0662	0.0689	0.0709	0.0714	0.0716	0.0715	0.0715
Benzene (V=5,5,2,2, 2,2,2 c.c. resptly)	Height	1.47	2.56	3.91	4.50	5.64	6.42	7.46
	Vh/t	0.0669	0.0791	0.0823	0.0841	0.0932	0.100	0.100

TABLE IV

Adsorbent : Kieselguhr.

Water (V=6, 5,5,2,5,2.5, 2.5,2.5 c.c. resptly.)	Height	1.71	2.12	3.52	4.20	5.46	6.23	7.34
	Vh/t	0.0579	0.0598	0.0634	0.0654	0.0658	0.0659	0.0659
MeOH (V=2c.c.)	Height	1.44	2.38	3.39	4.19	4.50	5.79	6.40
	Vh/t	0.0299	0.0354	0.0372	0.0388	0.0391	0.0402	0.0403
MeAc (V=5c.c.)	Height	1.54	2.89	3.92	4.50	5.16	6.68	7.24
	Vh/t	0.1374	0.1399	0.1415	0.1500	0.1541	0.1590	0.1599
Acetone (V=5c.c.)	Height	1.24	2.00	3.38	4.50	5.20	6.49	7.46
	Vh/t	0.110	0.113	0.126	0.132	0.146	0.151	0.153
Benzene (V=5 c.c.)	Height	1.82	2.02	3.02	4.23	4.50	5.40	6.50	7.28
	Vh/t	0.158	0.162	0.174	0.181	0.182	0.183	0.183	0.184

TABLE V
Adsorbent : MgO.

Water (V=5,5,5,2.5, 2.5,2.5,2.5, respctly)	Height	1.41	2.99	3.53	4.79	5.13	6.25	7.46
	Vh/t	0.053	0.056	0.059	0.060	0.060	0.060	0.060
MeOH (V=2.5 c.c.)	Height	1.15	2.42	3.47	4.02	5.46	6.82	
	Vh/t	0.0230	0.0428	0.0448	0.0450	0.0452	0.0.453	
MeAc (V=5 c.c.)	Height	1.95	3.04	4.45	5.73	6.83	7.44	
	Vh/t	0.246	0.271	0.296	0.307	0.312	0.315	
Acetone (V=5 c.c.)	Height	1.52	3.00	4.55	5.80	6.52	7.65	
	Vh/t	0.164	0.185	0.203	0.216	0.223	0.224	
Benzene (V=5 c.c.)	Height	1.62	3.40	4.52	5.73	6.93	7.26	
	Vh/t	0.0944	0.100	0.113	0.126	0.138	0.140	

DISCUSSION

The rate of flow of the solvents through variable heights of the columns of different adsorbents presents the following interesting characteristics :

(1) The rate of flow per unit time determined by V/t varies inversely as the height of the column under a constant pressure. But Vh/t becomes constant only after an optimum height of the adsorbent has been reached and this optimum height is attained in the neighbourhood of 4.5 cm. for most of the liquids flown through $CaCO_3$, silicic acid, Fuller's earth, and Kieselghur. The optimum heights for MgO column are, however, different for different liquids showing that the rate of flow is also much influenced by the nature of fluids and the adsorbent.

(2) Although V/t has been observed to decrease as the height of the column increases, an extremely interesting point arises in the fact that the values of Vh/t below the optimum height are slightly lower than the constant value of Vh/t obtained for the optimum height of the column. The constancy of this value of Vh/t for a particular solvent and adsorbent, however, is not affected beyond that optimum height within the range of our investigation (vide Tables I to V). It may be noted that the columns beyond a certain height have the risk of cracking from the lower layers according to our observations. Hence the height had to be maintained within a limit depending upon the nature of the adsorbent and the flowing liquid.

(3) The constant value of Vh/t is characteristic of the liquid flown and the adsorbent used. It can be generalised from the tables that polar molecules like water and MeOH have, a much lower value for Vh/t than the less polar or non-polar ones such as MeAc, acetone and C_6H_6. It is interesting to note that the comparative order of the constants (Vh/t) for H_2O and MeOH remains unaltered for all the adsorbents while that of C_6H_6, acetone and MeAc is affected by the nature of the adsorbent used (vide tables).

(4) In preparing the columns it was also observed that C_6H_6 formed bigger particles in the case of $CaCO_3$, MgO, silicic acid and Keiselghur, while in MeOH calcium carbonate gave finer suspensions which took longer time to settle.

The slight lowering of the value of Vh/t below the optimum height (vide tables) appears primarily to be due to the slight variations in the packing of the columns as we ascend from the lower to the higher layers. It may be visualised that the lower layers would be composed of finer particles than the upper zones of the column, with the result that there will be a slight

difference in the compactness of the lower region than that of the upper layers. The compactness, however, becomes more and more uniform with the height of the column, when the optimum height has been attained. This is evidenced by the fact that this optimum height for all the adsorbents except MgO comes up to 4.5 cm. for most of the liquids flown through these columns. The constancy in the value of Vh/t after the optimum height further suggests that the effect of pressure variations between the ends of the columns due to the packing conditions becomes negligible beyond the optimum height.

The other factors which affect the flow of the liquids through surface active columns are the forces of adhesion and cohesion which are considerably influenced by the polar and non-polar character of the adsorbent and the liquid. The presence of a polar group should increase the work of adhesion very much more than that of cohesion. In other words, the rate of flow should therefore depend upon the spreading coefficient of the liquid on the surface-active adsorbent. In the absence of other factors, the rate of flow should be greater for liquids having smaller spreading coefficient. This is evidenced by the rate of flow of liquids such as C_6H_6, acetone and MeAc compared to water and methyl alcohol.

The constancy in the value of Vh/t suggests further that it is fundamentally connected with the structure of the molecules which are oriented in a particular manner to the surface-active substance as they flow through the capillaries of the adsorbent columns. The degree of orientation *a priori* seems to depend upon (*i*) the polar and non-polar character of the liquid and the adsorbents and (*ii*) the net effect of forces of adhesion and cohesion at the interface of the liquid and the adsorbent.

Further work is in progress in these laboratories.

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THE USE OF SOME THIOGLYCOLLANILIDES IN INORGANIC ANALYSIS

By R. N. Misra and S. S. Guha Sircar

Ten thioglycollanilides have been synthesised from 10 aromatic primary amines, and tested for use in the detection of the common metallic radicals at different p_H ranges. The colour changes or precipitations were noted along with the solubilities of the precipitated complexes. Ag, Pb, Hg^{I}, Hg^{II}, Cu, Cd, Bi, Sn, Zn, Co and Ni gave insoluble complexes almost in all cases. Sensitivity limit for the cobalt complexes was about 0.5γ in most cases. Gravimetric estimations of cobalt with five compounds, and of silver with one compound have been made. The colorimetric analyses of the formation of two soluble cobalt complexes derived from *o*- and *m*-aminobenzoic acid compounds have also been carried out.

Among organic salinogenic reagents, the mercapto compounds form a very active series by virtue of the remarkably acidic -SH group. One such compound, the thioglycollic acid anilide, was found by Bersin to give a voluminous red precipitate with cobalt (*Z. anal. Chem.*, 1931, **85,** 428). Berg *et al.* discovered another more useful reagent, 'thionalide', which could be used in gravimetric, iodimetric, colorimetric, nephelometric and certain micro-analyses (*ibid.*, 1938, **112,** 161 ; 1939, **117,** 241). Two other thioglycollanilides, *p*-(mercaptoacetamido)-acetophenone and *o*-(mercaptoacetamido)-*p*-nitrophenol, were prepared and tested more recently by Ubeda (*Chem. Abs.*, 1950, **44,** 3926[d]; 1951, **45,** 5073[h], 7963[c]; 1952, **46,** 10044[a]; 1954, **48,** 2524[a]). In the present paper the preparation, properties and analytical uses of ten new thioglycollanilides have been described.

Experimental

The thioglycollanilides have been prepared by (*i*) alkaline hydrolysis of carbamyl thioglycollanilides (Beckurts and Frerich, *J. prakt. Chem.*, 1902, *ii*, **66,** 174), (*ii*) by the saponification of acetothioglycollanilides (Benary, *Ber.*, 1913, **46,** 2105), (*iii*) by the condensation of thioglycollic acid or α-acetylmercaptoacetyl chloride with the appropriate amine hydrochloride in presence of quinoline (*Chem. Abs.*, 1947, **41,** 1701), or (*iv*) by refluxing a mixture of equivalent quantities of thioglycollic acid and the appropriate amine in benzene for a period of 9 hours (Van Allan, *J. Amer. Chem. Soc.*, 1947, **69,** 2914).

The method used in the present work is more simple and time-saving, and consists in heating of an equimolecular mixture of thioglycollic acid and the appropriate amine in a $1'' \times 6''$ test tube in a glycerine bath, maintained at 110°—120°, in a slow current of CO_2. The heating is continued for about 2-2½ hours till the melt solidifies, or a drop of it solidifies when cooled to room temperature or stirred into 1-2 c.c. of water. The whole melt is then poured into a beaker of water and stirred well till the solid separates in lumps. These are powdered and washed with dilute HCl and water to remove unchanged amine and thioglycollic acid respectively. Further purifications were made by repeated recrystallisations from dilute alcohol.

The amines used in the present work were sulphanilamide, sulphapyridine, sulphathiazole, *m*-nitroaniline, *o*-chloroaniline, *o*-and *m*-aminobenzoic acids, benzocaine and DADPS. Table I records the m.p., analytical data and some properties of the thioglycollanilides.

TABLE I

[M denotes NH. CO. CH_2. SH ; sol, soluble ; sp, sparingly and alc, alcohol]

Serial No.	Compounds.	M.P.	% Sulphur. Found.	Calc.	Nature of the compounds.
A_1	*p*-M-benzene sulphonamide	201-202°	25.8	26.02	White needles; insol. in cold water or dil. HCl; sol in alc.
A_2	N^4-Thioglycollyl sulphapyridine	195°	20.5	19.82	Do
A_3	N^4-Thioglycollyl sulphathiazole	197°	29.36	29.18	Do
A_4	*m*-M-nitrobenzene	91-92°	14.89	15.1	Pale pink cryst.; sol in cold NH_4OH, NaOH, hot water and dil. HAc; highly sol in alc; on keeping darkens.
A_5	*o*-M-chlorobenzene	61°	15.95	15.87	White needles with disagreeable odour; insol. in dil. HCl, HAc, NaOH ; highly sol in alc, or acetone.
A_6	*m*-M-benzoic acid	210°	15.34	15.17	White cryst.; insol. in dil. acid; sol in dil. alkalies and alc ; liberates CO_2 from $NaHCO_3$ soln.
A_7	*o*-M-benzoic acid	159°	15.24	15.17	Do
A_8	*p*-M-ethyl benzoate	105°	13.88	13.39	Do. No CO_2 from $NaHCO_3$ soln.
A_9	*p*-M-*p'*-aminodiphenylsulphone	130°	19.00	19.87	Greyish white powder; darkens on keeping; sp sol in dil. HCl or alkali ; highly sol in alc and acetone.
A_{10}	*pp'*-Di M-diphenylsulphone	145°	23.33	24.24	White powder; insol. in dil. HCl or HAc; sp sol in dil. alkali ; sol in alc to a less extent.

Use in Qualitative Analysis

Stock solutions of (*i*) molar solutions of a soluble salt of each of Ag, Pb, Hg (ous & ic), Cu^{II}, Cd, Bi, As, Sb, Sn^{II}, Fe^{III}, Al, Cr, Mn, Zn, Co, Ni, Ca, Ba, Sr, Mg, MoO_4^{2-}, WO_4^{2-} and of (*ii*) NaAc—HAc buffers of p_H 3.42, 4.05, 4.99 and 5.89 were prepared. Two c.c. of a buffer solution, 5 drops of a salt solution, 10 drops of a freshly prepared 1% alcoholic solution of the reagent were shaken well and the colour change or precipitation was observed in cold and on heating. The precipitates were filtered through small funnels, washed several times with water, and their solubilities in different solvents were tested. When the reagent itself came down (due to dilution of the alcoholic solution), it was soluble in dilute alcohol. In doubtful cases, the well washed precipitates were decomposed by dilute acids, and tests for the particular cations made by known methods. For testing completeness, of precipitation a slight excess of the reagent was added to the filtrate and the mixture was heated on a water-bath for ½ hour, the contents were cooled, filtered, and the filtrate was tested for the absence of the cation by known reagents. Results of qualitative analyses are recorded in Table II.

TABLE II

[Q denotes quantitative ; sol, soluble ; sp, sparingly ; Ammon, Ammonical ; EtAc, ethyl acetate. Colours mentioned indicate colour of ppts., unless 'color' is written].

Serial No. of reagent.	Ions.	p_H.	Colour of ppt. or soln.	Nature of complexes and whether quantitative.
A_1	Ag	3.42-7.0	Pale yellow	Q. Insol in water, dil. HAc, alc, acetone ; sol in conc. HNO_3 giving yellow soln. ; decomp on heating or long keeping.
	Hg^{I}	,,	White	Not Q. Decomp. on heating or keeping. Insol in water alc, acetone and HAc ; sol in conc. HNO_3.
	Hg^{II}	,,	Do	Q on digestion at 100° ; insol in water, alc, acetone, HAc & dil. HNO_3 .
	Co	,, & ammon.	Dark pink	Q from faintly ammon. soln. ; unaffected by dil. HCl & HAc or heat (130°). Insol in water ; sp sol in 96% alc, conc. NH_4OH, hot HAc & EtAc ; complete decomp. by conc. HNO_3 or HCl.
	Ni	(ammon.)	Brown	Not Q. Insol in water, cold dil. alc, or acetone ; sol in dil. acids.
	MoO_4^{2-}	3.42-4.99	Green-blue color	Reduction of Mo^{VI}.
A_2	Ag	3.42-7.0 & ammon.	Pale yellow Do : turns brown	Q. Insol in H_2O, alc, acetone, dil. HAc ; decomp. by conc. HNO_3.
	Hg^{I}	3.42-7.0	White	Not Q. Insol in H_2O, alc, dil. HAc; decomp. on keeping or heating.
	Hg^{II}	,,	Do	Q. Insol in H_2O, alc ; sol in conc. HNO_3 or HCl.
	Cu	,, (ammon.)	Grey Black-brown	Q & granular at p_H 4.99-5.89. Insol in H_2O, alc.
	Cd	3.42-7.0	White	Insol in water or alc.
	Co	4.05-7.0 & ammon.	Pink Dark pink	Q from faintly ammon. soln. Insol in H_2O, alc, acetone, amyl alc, dil. acids ; decomp. by conc. HNO_3.
	Ni	4.05-7.0 & ammon.	Grey	Not Q. Insol in H_2O, alc or dil. HAc.
	MoO_4^{2-}	3.42	Blue color	Reduction of Mo^{VI}.
A_3	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in H_2O, alc, HAc, or acetone ; decomp. by conc. HNO_3.
	Pb	3.42-7.0	White	Do
	Hg^{I}	,,	Grey	Do Decomp at 100°.
	Hg^{II}	,,	White	Do No decomp.
	Cu	4.05-7.0 (ammon.)	Purple Brown	Q at p_H 4.05-5.89. Decomp. at 100° ; insol in alc, acetone, dil. HAc ; sol in dil. mineral acids.
	Cd	3.42-7.0	White	Q. Insol in alc, acetone, dil. HAc.
	Bi	,,	Dirty white	Not Q. Insol in alc, acetone ; sol in hot dil. or conc. HCl.
	Co	3.42-4.05 4.99-7.0 & ammon.	Faint pink Pink-brown	Q & voluminous from ammon. soln. sp sol in 96% alc, cold dil. alc, acetone, dil. HAc ; decomp. by conc. HCl or HNO_3.
	Ni	3.42-4.05 4.99-7.0 & ammon.	Faint grey Grey	Not Q. Insol in H_2O & dil. alc ; decomp. by dil. mineral acids.
	MoO_4^{2-}	3.42 4.05-4.99	Blue colour Yellow color	Reduction of Mo^{VI}.

TABLE II (contd.)

Sr. No.	Ions.	p_H.	Colour of ppt. or soln.	Nature of complexes & whether Q.
A_4	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in H_2O, alc ; sol in hot dil or cold conc. HNO_3; decomp. at 100°.
	Pb	3.42-7.0	,,	Do. No decomp. at 100°.
	Hg^{I}	,,	Brown	Q. Insol in H_2O, alc, acetone, dil. HAc; decomp. at 100°.
	Hg^{II}	,,	White	Q. Insol in H_2O, alc, acetone, dil. HAc ; sol in cold conc. or hot dil. HCl or HNO_3.
	Cu	3.42-4.05 (ammon.)	Black ,,	Insol in H_2O, alc, acetone, dil. HAc ; decomp. by mineral acids.
	Bi	3.42-7.0	Dirty white	Do Do
	Sn	4.99-5.89	White	Insol in water & alc.
	Co	4.05	Faint pink	Q. Insol in H_2O, dil. alc, acetone, HAc, EtAc; readily sol in hot conc. HCl or HNO_3.
		4.99-7.0 & ammon.	Dark pink	
	Ni	4.05	Faint brown	
		4.99-7.0 & ammon.	Brown	Not Q. Insol in H_2O, alc, dil. HAc ; sol in hot dil. mineral acids.
	Zn	4.99-5.89	White	Q. Do Do
	MoO_4^{2-}	3.42-4.05	Yellow	Not Q ; sol & turns blue on heating.
A_5	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in H_2O, alc, acetone ; sol in conc. HNO_3 ; decomp. at 100°.
	Pb	3.42-7.0	Pale yellow	Not Q. Do Do ; no decomp.
	Hg^{I}	,,	Grey	Granular at p_H 4.99-5.89 ; decomp at 100°.
	Hg^{II}	,,	White	Q. Insol in H_2O, alc, or dil. HAc.
	Cu	(ammon.)	Dull grey Brown	Do
	Bi	3.42-4.05	Yellow	Q at p_H 3.42-4.05. Insol in H_2O ; but sol in alc.
		7.0	,,	
		4.99-5.89	Yellowish brown	
	Co	3.42-4.05	Pale pink	Q from ammon. soln. Insol in H_2O, alc, acetone, HAc,
		4.99-7.0 & ammon.	Dark pink	dil. mineral acids, cold conc. HCl or HNO_3.
	Ni	4.99 & 7.0	Faint grey	
		5.89 & ammon.	Grey	Fairly Q. Insol in H_2O, alc ; sol in dil. mineral acids.
	MoO_4^{2-}	3.42	Yellow	Not Q. Sol & turns blue on heating ; reduction of Mo^{VI}
		4.05-5.89	Blue colour	
A_6	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in alc, acetone, dil. or glacial HAc; sol in conc. HNO_3.
	Pb	3.42-7.0	White	Insol in H_2O or alc.
	Hg^{I}	,,	Grey	Q. Decomp on heating or keeping.
	Hg^{II}	,,	White	Q. Insol in HAc, alc, acetone, dil. HNO_3; sp sol in hot dil. HCl, EtAc ; sol in conc. HCl & HNO_3.
	Cu	3.42-4.99	Greyish white	Q at p_H 5.89.
		5.89-	Do brown	
		7.0	Do white	
		(ammon.)	Brown color	Color deepens on keeping.
	Cd	3.42-7.0	White	Q at p_H 4.99-5.89 & granular ; insol in alc, acetone, EtAc ; sol in HCl, HNO_3.
	Bi	3.42-7.0	Pale yellow	Q & ganular at p_H 3.42-4.99. Do.
	Sn	,,	White	Not Q. Insol & sol in HCl, HNO_3.
	Fe	3.42-4.05 & 7.0	Blue color	Immediate blue; discharged quickly to white ppt.;
		4.99-5.89	Brown	brown ppt not Q.
	Zn	4.05-5.89	White	Q. Insol in H_2O, alc, acetone ; sol in dil. HAc, HCl, HNO_3 & EtAc in cold.
	Co	4.05-5.89 (ammon.)	Pink Blood-red color	Ppt. colloidal, not Q ; color is not extractible with ether, or EtAc.
	Ni	4.05-5.89 (ammon.)	Grey Brown colour	Ppt. not Q ; insol in alc; color not extractible with ether, EtAc.
	MoO_4^{2-}	3.42-5.89	Yellowish green to Blue color.	Reduction of Mo^{VI}.

TABLE II (contd.)

Sr. No.	Ions.	p_H.	Colour of ppt. or soln.	Nature of comlexes & whether Q.
A_7	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. insol in alc or HAc; decomp. at 100°.
	Pb	3.42-7.0	White	Q. Insol in alc, dil. HAc.
	Hg^{I}	,,	Grey	Do Decomp. at 100.°
	Hg^{II}	,,	White	Not Q. Sp sol in alc.
	Cu	3.42 & 7.0	Faint grey	Not Q; insol in alc, dil. HAc.
		4.05-4.99-5.89	Grey Do-(& blue color)	
		(ammon.)	Brown	
	Cd	3.42-7.0	White	Do
	Bi	,,	Pale yellow	Q at p_H 3.42; insolin alc, dil. HAc.
	Sn	,,	White	Insol in alc, dil. HAc.
	Fe	3.42-4.05 & 7.0	Blue color	Blue color disappears quickly to white ppt; not Q; insol in alc.
		4.99-5.89	Black-grey	
	Zn	3.42-7.0	White	Not Q. Insol in alc and dil. HAc.
	Co	4.99-5.89 & ammon.	Blood-red color.	Not extractible with ether, EtAc; stable towards dil. mineral acids.
	Ni	4.99	Grey	Ppt. not Q; color not extractible with ether, EtAc.
		5.89 (ammon.)	Brown color Pink ,,	
	MoO_4^{2-}	3.42-4.99	Yellow ,,	Reduction of Mo^{VI}.
A_8	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in H_2O, alc, acetone, dil. HAc; decomp. at 100°.
	Pb	3.42-7.0	Do	Insol in alc, acetone, dil. HAc.
	Hg^{I}	,,	Grey	Decomp. on heating or keeping.
	Hg^{I}	,,	White	Q. Insol in alc, acetone, HAc; sol in conc. HNO_3 or HCl (cold.).
	Cu	3.42	Yellow	Not Q. Do
	Bi	3.42-7.0	Pale yellow	Do
	Sn	4.99-5.89	White	Do
	Zn	4.05-5.89	White	Do
	Co	3.42-7.0 (ammon.)	Pink Dark pink	Q in ammon. Do. Sol in hot conc. HCl, HNO_3.
	Ni	3.42-7.0 (ammon.)	Grey Greyish brown	Voluminous at p_H 4.99, 5.89 & ammon; insol in alc, acetone, HAc.
	MoO_4^{2-}	3.42-4.05	Yellow	Sol on heating; becoming blue on keeping.
A_9	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in alc, acetone, dil. HAc; decomp at 100°.
	Pb	3.42-7.0	Pale yellow	Q. Insol in alc or acetone.
	Hg^{I}	,,	Grey	Q. Decomp. at 100°.
	Hg^{II}	,,	White	Q. Insol in alc, or acetone or dil. HAc
	Cu	3.42	Pale yellow	Not Q. Do
	Cd	3.42-7.0	White	Do
	Bi	,,	Dirty white	Do
	Co	,, (ammon.)	Pink Dark pink	Q from ammon. soln. Insol in alc, acetone, HAc & dil. mineral acids.
	Ni	3.42-7.0 & ammon.	Brown	Volumnious but not Q in ammon soln. Sp sol in hot H_2O, alc, dil. HAc.
	MoO_4^{2-}	3.42-5.89	Yellow	Not Q. Sol in hot H_2O giving blue soln.

TABLE II (contd.)

Sr. No.	Ions.	p_H	Colour of ppt. or soln.	Nature of complexes & whether Q.
A_{10}	Ag	3.42-7.0 (ammon.)	Pale yellow Yellow	Q. Insol in alc, acetone, dil. HAc ; decomp. at 100°.
	Pb	3.42-7.0	Pale yellow	Q. Insol in alc, acetone, dil. HAc.
	Hg^{I}	,,	Grey	Decomp. on water-bath.
	Hg^{II}	,,	White	Insol in alc & dil. HAc.
	Cu	3.42-4.99	Yellow	Not Q. Insol in alc.
	Cd	3.42-70	White	Insol in alc & dil. HAc.
	Bi	,,	Dirty white	Do
	Sn	4.05-7.0	White	Do
	Zn	3.42-5.89	Do	Do
	Co	3.42-7.0 (ammon.)	Pink Pinkish brown	Q & voluminous in ammon. soln. ; insol in alc, acetone. HAc or dil. mineral acids.
	Ni	3.42-7.0 (ammon.)	Brown Greyish brown	Voluminous from ammon. soln. ; insol in alc.,
	MoO_4^{2-}	3.42-5.89	Yellow	Not Q. Sol on heating giving blue colour

Use in Gravimetric Analysis

Estimation of Cobalt.—A known volume of standard $CoSO_4$ solution ($M/10$ approx.) was taken in a 400 c.c. tall beaker. About 0.5 g. of NH_4Cl, 5 drops of H_2O_2, and several drops of NH_4OH were added to it till it was distinctly alkaline. The mixture was gently heated till the effervescence almost had ceased, then diluted to about 100 c.c. and to the hot solution an 1% alcoholic solution of the reagent was added dropwise till a slight excess had been added with constant stirring. The contents were digested on a water-bath for 3-4 hours, then cooled to room temperature, filtered through a weighed sintered crucible, washed first with very dilute hot alcoholic solution till the precipitate was transferred and then with hot water for several times till the filtrate was free from SO_4^{2-} and Cl^-, and dried in an electric oven at 125°-130° to a constant weight.

Composition of the Cobalt Complexes.—The cobalt complex of compound A_8 was precipitated as above and dried at 100°. A known weight of this was decomposed in a porcelain crucible with conc. HNO_3 and ignited to Co_3O_4. Results of analysis show 0.084 g. of complex to yield 0.0385 g. of Co_3O_4 leading to the proportion, reagent : Co as 3.1 : 1.

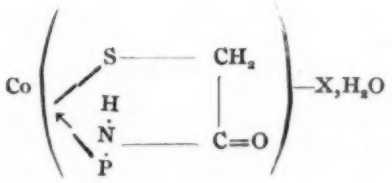
Besides the decomposition studies, the weight of the complexes obtained quantitatively from a known amount of $CoSO_4$ solution corresponded to the above proportion of Co : reagent. Table III record the results of estimations of cobalt assuming the composition of cobaltic complex.

TABLE III

Sr. No. of reagents	Co present in soln.*	Temp. of drying.	Wt. of complex.	Co found assuming cobaltic complexes.
A_1	0.0296 g.	110°	0.4021 g. 0.4023	0.0298 g.
A_2	,,	130°	0.5209 0.5212	0.0294
A_4	0.0148	110°	0.1687 0.1689	0.0144
A_5	0.0153	110°	0.1700 0.1706	0.0152
A_8	0.0306	110°	0.4023 0.4027	0.030

*Amount of Co present in the solution was determined by gravimetric estimation of SO_4^{2-} (indirect method) and by α-nitroso-β-naphthol.

The above results lead to the conclusion that a cobaltic complex is formed which may be formulated as :



(where P represents the phenyl or substituted phenyl group).

Estimation of Silver.—Most of the silver complexes of the thioglycollanilides were quantitatively precipitated from the solution but decomposed on heating on a water-bath. The complex from the compound A_3, however, did not decompose easily and the precipitate was more granular. Decomposition to metallic silver and also the weight of the quantitative precipitates from a known volume of standard $AgNO_3$ solution suggest the complex to have the composition $Ag(C_{11}H_{10}O_3N_3S_3)$, H_2O (%of Ag found, 24.15 ; calc., 23.7). A similar complex has been reported by Ubeda (*loc. cit.*).

Sensitivity Tests

The sensitivity tests for the Co and Ni complexes of the thioglycollanilides have been made. The results are shown in Table IV.

TABLE IV

	A_1.	A_2.	A_3.	A_4.	A_5.	A_6.	A_7.	A_8.	A_9.	A_{10}.
				Cobalt complex.						
PL × 10^3	1.0	1.0	1.0	1.0	1.0	-	-	1.0	1.0	1.0
CL × 10^5	5.0	5.0	5.0	1.0	1.0	5.0	5.0	1.0	1.0	10.0
IL (in γ)	0.5	2.5	0.5	0.25	0.5	0.5	0.5	0.5	2.5	2.5
				Nickel complex.						
PL × 10^3	1.5	1.5	1.5	1.5	1.5	-	-	1.5	1.5	0.75
CL × 10^5	-	-	-	0.75	0.75	0.75	0.75	0.75	0.75	0.5
IL (in γ)	147.5	147.5	147.5	14.75	14.75	14.75	29.5	37.0	14.75	14.75

[PL denotes precipitation limit ; CL, coloration limit and IL, identification limit].

Colorimetric Analysis

The formation of the deeply coloured cobalt complexes of compounds A_6 and A_7 was studied colorimetrically. The development of colour in each case was found to be complete within half an hour, and at p_H about 10. The measurements were carried out with a grating type 'Unicam' photoelectric colorimeter working between the range 400 and 700 mμ. The results of variation of transmittance for A_6 and A_7 with wave-lengths were plotted graphically in Fig. 1, and a maxima in each was obtained at wave-lengths 625 mμ and 630 mμ.

The validity of Beer's law was tested over a range of wave-lengths and most linear relationships were obtained at about the wave-lengths of maximum transmission. Tables V and VI record the results for A_6 and A_7 respectively.

Fig. 1

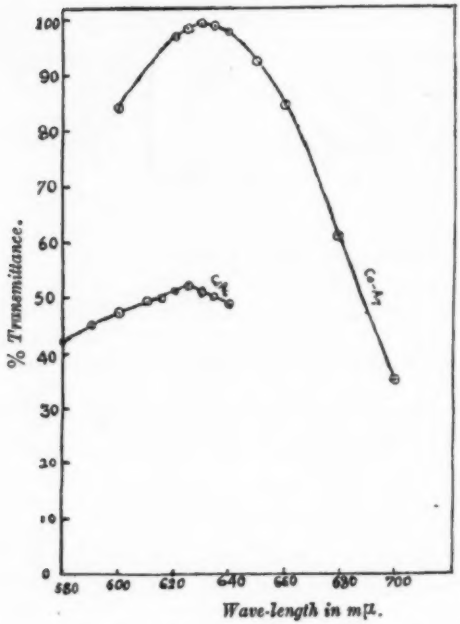


TABLE V

Co no. of Co.	Extinction.
0.001 *M*	0.34
0.0005	0.165
0.00025	0.08
0.000125	0.05
0.0001	0.045

TABLE VI

Conc of Co.	Extinction.
0.001 *M*	0.13
0.0008	0.0975
0.0004	0.055
0.0002	0.02
0.0001	0.01

The plots of the concentration of Co against extinction give straight lines showing that the production of colours is in agreement with Beer's law.

Fig. 2 (625 mμ)

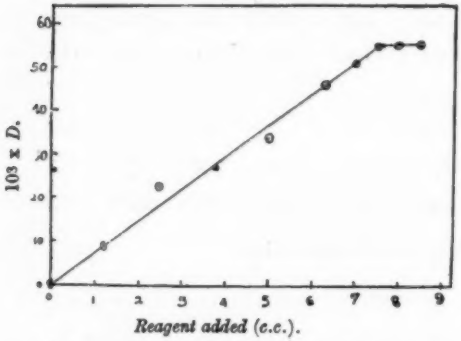
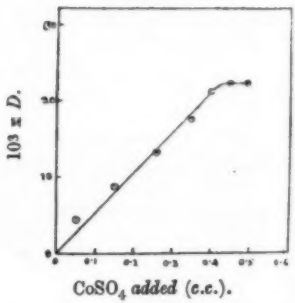


Fig. (630 mμ)



Colorimetric titrations of cobalt against the reagents suggest the complex to contain Co : reagent in the ratio of 1 : 3, a proportion agreeing with the gravimetric analysis of a similar complex. Figs. 2 and 3 $CD = \log_{10} I_0/I_2$ show the results of titrations.

Further investigations are in progress.

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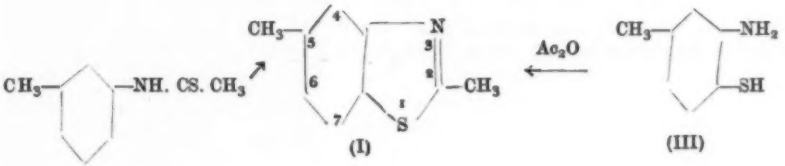
A NOTE ON THE PREPARATION OF 2 : 5-AND 2 : 7-DIMETHYLBENZTHIAZOLES

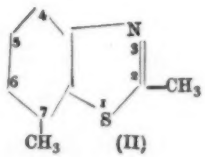
By J. C. Banerji

Of the four possible 2 : 4-, 2 : 5-, 2 : 6- and 2 : 7- dimethylbenzthiazoles, first three have been described in literature. 2 : 6-Dimethylbenzthiazole was prepared by Jacobson and Ney (*Ber.*, 1889, **22**, 907) by the oxidative cyclisation of thioaceto-*p*-toluidide with alkaline potassium ferricyanide. 2 : 4-Dimethylbenzthiazole was prepared by Kiprianov and Sitsch (*Chem. Abs.*, 1938, 4167) analogously from thioaceto-*o*-toluidide.

While the products of the cyclisation in the above two cases are single and unambiguous, similar treatment of thioaceto-*m*-toluidide may yield 2 : 5-(I) or/and 2 : 7-dimethylbenzthiazole (II).



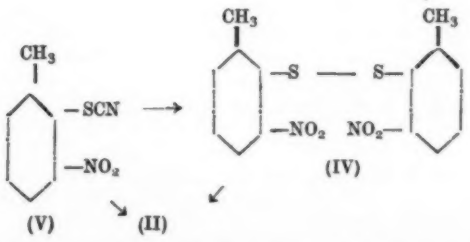
(I) (III)



(II)

It has now been found that thioaceto-*m*-toluidide on oxidation with alkaline potassium ferricyanide yields mainly (I) which is identical with that prepared by Kiprianov and Sitsch (*loc.cit.*) from 2-amino-4-methylthiophenol (III) and acetic anhydride, as confirmed by the m.p. of the ethiodides.

2 : 7-Dimethylbenzthiazole (II), which was hitherto unknown, was sought to be prepared by the way of the disulphide (IV) by its reductive cyclisation with zinc dust, acetic acid and acetic anhydride according to the well known method of Kõnig and Siedel (*Ber.*, 1928, **61**, 2068). Although the disulphide (IV) has been prepared by Bogert and Allen (*J. Amer. Chem. Soc.*, 1927, **49**, 1320) by the aerial oxidation of an alkaline solution of 3-nitro-2-thiocyanotoluene (V), attempts to repeat their experiment have been so far fruitless. However,



it was soon discovered that the isolation of the disulphide was not imperative at all, as the

required thiazole was obtained directly in good yield from the thiocyanotoluene (V) by its reductive cyclisation with zinc dust, acetic acid and acetic anhydride.

2 : 5-*Dimethylbenzthiazole.*—Thioaceto-*m*-toluidide (7 g.) was dissolved in 100 c.c. of 20% NaOH solution, and 10 c.c. of 20% potassium ferricyanide solution were added to it. The viscous mass that settled at the bottom after 24 hours was extracted with ether and the ether extract was dried over anhydrous K_2SO_4. On distillation *in vacuo*, the thiazole was obtained as a pale brown oil, yield 32%, b.p. 142°-146°/10 mm. Its ethiodide had m.p. 195-96°. Kiprianov and Sitsch (*loc. cit.*) also record the m.p. of the ethiodide as 195-96°.

2 : 7-*Dimethylbenzthiazole.*—3-Nitro-2-thiocyanotoluene (6 g.) was dissolved in boiling glacial acetic acid (50 c.c.) and acetic anhydride (25 c.c.) and zinc dust (30 g.) were slowly added to the boiling solution till the solution became nearly colorless. The solution was filtered through glass wool and the filtrate on being made alkaline with a strong solution of caustic soda, the thazole separated as a thick oily liquid. It was purified by steam distillation. The base was taken up from the distillate with ether which on evaporation left a pale yellow oil (1.3 g.). The picrate crystallised from alcohol in yellow needles, m.p. 138°. (Found : C, 45.4 ; H,3.0. $C_{15}H_{12}O_7N_4S$ requires C, 45.9 ; H,3.0 per cent). The chloroplatinate on ignition left Pt, 26.59 %. $(C_9H_9NS)_2H_2PtCt_6$ requires Pt, 26.51 %.

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Dr. Shanti Swarup Bhatnagar, Kt., D.Sc., F.R.S., F.N.I.

Born: Feb. 21, 1894. *Died:* Jan. 1, 1955.

Chemists in India mourn today the sudden and untimely death of Dr. Shanti Swarup Bhatnagar, which took place at his residence on 1st January, 1955, at 8-30 p.m. Dr. Bhatnagar was hale and hearty on the 31st December, 1954, and not only attended to his normal work, but gave a nice evening party to his friends, Indian and foreign, at his Farm House, and a dinner at home. The same night he got an heart-attack from which it seemed he had recovered, but the second one which came next evening proved fatal.

The Indian Chemical Society has suffered a heavy loss in his death. He was one of the three founders, "The Three Musketeers" as Acharya P. C. Ray called them, of the Society which was established in 1924, with Acharya Ray as its first President. In the beginning Dr. Bhatnagar worked as a member of the Council of the Society and did his best to promote the aims and objects of the Society and to place it on sound economic footing. He was elected President of the Society during 1941-42 and delivered the Acharya P. C. Ray Memorial Lecture in 1951. To commemorate the seventieth birthday of Acharya Ray, he had offered for several years the award of a Gold Medal to the Junior Research Chemist for his best work published in the Journal of the Society.

Shanti Swarup was born on 21st February, 1894, at Bhera in the district of Shahpur in the Punjab. His father, the late Munshi Parmeshri Sahai, having died when he was only eight months old, his childhood was passed at Sikandrabad under the guardianship of his maternal grandfather, the late Munshi Pearey Lal (one of the first to have qualified at the Roorkee College of Engineering) who had settled there on retirement. His early education was also conducted at the Anglo-Vernacular School in the same town.

In 1908 Shanti Swarup shifted to Lahore for his high school and college education. This was done at the instance of the late Rai Sahib Lala Raghunath Sahai, a dear friend of his late father and then Headmaster of Dayal Singh High School. Shanti Swarup passed the Matriculation Examination in 1911 and F.Sc. in 1913, both in first division. In 1916 he took his B.Sc. with Honours in Physics, and M.Sc. in Chemistry in 1919 with the highest marks in Physical and Inorganic Chemistry, both from the Forman Christian College, Lahore. For part fulfilment of the M.Sc. Degree Examination Shanti Swarup submitted a thesis on "The Effect of Adsorbed Gases on the Surface Tension of Water".

In August, 1919, Bhatnagar left for England on his way to America. Finding no passage for the States, he joined the Ramsay Laboratories of the University College, London, and worked under Professor F. G. Donnan for the D.Sc. Degree, which he obtained in 1921. The title of his thesis was "The Solubilities of bi-and trivalent Salts of Higher Fatty Acids in Oils and their Effect on the Surface Tension of Oils". This work has been described by Clayton in his book on "Emulsion and Emulsification" under the title "Bhatnagar's Researches".

While working in London, he was awarded a five-year Travel Scholarship by the Privy Council of Scientific and Industrial Research, which he availed of only for a year. After taking the D.Sc. Degree, he went to Berlin and worked for some time at the Kaiser-Wilhelm Institute with Professors Haber and Freundlich.

On his return to India in 1921, Dr. Bhatnagar joined the Banaras Hindu University as University Professor and Head of the Department of Chemistry. He had actually received the appointment letter while still in England, from Pandit Madan Mohan Malaviya, the Vice-Chancellor of the University. During his three years' stay at Banaras he attracted keen young students from all parts of India, enthused them with the spirit of research, and established a good school in Colloidal Chemistry. It was here that he advocated the Physico-Chemical Theory of Adsorption and commenced his studies on the mechanism of formation of Liesegang rings, even in such systems as ringworms and beetroot. In order to concentrate on his research and teaching work Dr. Bhatnagar left the normal routine administration of the Department to his colleague, Professor M. B. Rane, who was doing that work before he came to the University.

In 1924 Dr. Bhatnagar was invited to Lahore to be the first Director of the newly established University Chemical Laboratories. Here also, research students sought admission to his laboratory in large numbers, and received training and guidance in research under this forceful and inspiring teacher. Besides pursuing his work in Colloidal Chemistry, Dr. Bhatnagar initiated in this laboratory new investigations on important problems in other fields. Amongst these the largest contribution has been made to Magnetochemistry, for which these laboratories were pioneers in India, and won international recognition. It was here that the Bhatnagar-Mathur magnetic interference balance was designed, and was later manufactured by Messrs. Adam Hilger, London. Bhatnagar, in collaboration with his pupil Dr. K. N. Mathur, wrote a book entitled "Physical Principles and Applications of Magnetochemistry" in 1935. This work is published by MacMillan & Co., and is recognised as a standard work on the subject in English, and has been adopted by foreign universities.

Dr. Bhatnagar's standing as one of the foremost Colloidal Chemists in India received a great recognition when he solved in a masterly fashion the problem with which the Attock Oil Company of Rawalpindi were faced in their drilling operations for oil. In gratitude to Dr. Bhatnagar, M/s. Steel Brothers offered him a sum of Rs. 1,60,000; this was later increased to Rs. 4,00,000 and was awarded by the Punjab University in the form of six Research Scholarships for work on subjects of interest to petroleum industry. Prior to this, Dr. Bhatnagar had already commenced working on problems relating to Applied and Industrial Chemistry, including work on the utilization of waste products, under schemes put forward by some leading industrialists.

In 1940 the Government of India had set up a Board of Scientific & Industrial Research with a view to increasing India's industrial activity and meeting the great demand for industrial products, created by the War. Dr. Bhatnagar was invited by the Government to be its first Director. The immense work conducted under his able guidance at the laboratories, situated at first in Calcutta and later on shifted to Delhi, was highly appreciated and has been a valuable contribution not only towards the furtherance of war effort but also in the peace-time economy of the country.

In 1942 the Government of India created the Industrial Research Fund and set up an autonomous body, the Council of Scientific & Industrial Research, to administer it. At this time Dr. Bhatnagar prepared a plan for the creation of five National Laboratories under the aegis of the Council; this plan was subsequently extended to cover ten more laboratories and institutes in its scope.

After the war was over and India became independent, the Government of India created a Ministry of Natural Resources and Scientific Research and appointed Dr. Bhatnagar as its first Secretary. He discharged simultaneously the duties of the Secretary to the Ministry and of the D.S.I.R. Dr. Bhatnagar realised that time was then opportune to put his plan of the chain of National Laboratories into action, and immediately proceeded to execute it. It is remarkable that under his dynamic guidance and forceful organization twelve of these laboratories came into existence and commenced their planned work in full swing within a short period of seven years. This unique and unparalleled achievement of Dr. Bhatnagar would go down in history as one of the wonders and would bring honour not only to him but to the country

as well. The Prime Minister's appreciation of Dr. Bhatnagar's work can be seen from his observation : "Dr. Bhatnagar was a special combination of many things, added to which was a tremendous energy, with an enthusiasm to achieve things. The result was that he left a record of achievement which was truly remarkable. I can truly say that but for Dr. Bhatnagar, you could not have seen today the chain of these National Laboratories." It should not be forgotten that behind Dr. Bhatnagar's successes was the inspiring and guiding hand of our Prime Minister. Sir C. V. Raman has rightly remarked : "Such magnificent progress in the development of scientific research, and early realization of India's ambitious plans have only been possible due to Nehru-Bhatnagar effect."

Another equally important achievement of Dr. Bhatnagar is the establishment of the National Development Corporation of India for the translation of the results of laboratories to large-scale commercial exploitation. This is a proof of the foresight of Dr. Bhatnagar, of his brilliance as a thinker, and of his devotion to the cause of the uplift of our country. Dr. Bhatnagar was also mainly responsible for the establishment of "The India Rare Earths Ltd." factory at Alwaye, in Travancore, and constituted a 'one-member committee' for conducting negotiations for the establishment of three oil refineries in India. One of these has already commenced production.

Dr. Bhatnagar's gigantic work has been recognised and appreciated both in India and abroad. The Government of India conferred on him the title of O.B.E. in 1936, and he was created a Knight in 1941. On Independence Day the Government awarded him the title of "Padma Vibhushan" (Dusara Varg) in 1954. In 1943 he was elected to the Fellowship of the Royal Society and an Honorary Fellow and, later, Vice-President of the Society of Chemical Industry, London. He had the unique honour of being elected twice in 1928 and 1938 as President of the Chemistry Section of the Indian Science Congress. He was elected as General President of the Indian Science Congress in 1945, and President of the National Institute of Sciences, India, in 1949. Universities of Oxford, Patna, Allahabad, Delhi, Banaras, Lucknow, Agra and Saugor, awarded Honorary Doctorate Degrees to him. Recently the Government appointed him as Chairman of an important Statutory Body, the University Grants Commission.

Dr. Bhatnagar had travelled a lot both in India and abroad. He was sent as a delegate in 1923 to the Annual Meeting of the British Association held at Liverpool and again in 1931 to the British Association Centenary and Faraday Centenary. He attended the Empire Universities Congress in 1931 at Edinburgh and in 1936 at Cambridge. He went in 1944 as a member of the Goodwill Mission to the United Kingdom and the United States of America and again in 1946 as a leader of the Delegation of Indian Scientists to the British Commonwealth Scientific Conference. During the last six or seven years he must have made several trips to Europe and the United States in connection with special assignments, the last one being in April, 1954.

Dr. Bhatnagar was a gifted administrator and an able organizer and worked hard to pursue the programme of work which he undertook. In his speech delivered at the inauguration of the National Physical Laboratory, our Prime Minister said"... Dr. Bhatnagar has certain qualities which I, for one, admire very greatly, and that quality is to get things done. It is a quality which, I regret to say, most people lack. We talk a lot about theories and philosophies, and what should be done, and what might be done and what ought to be done. But somehow, all that is not translated into things that are done. Dr. Bhatnagar has that quality of translating the odds into what has been done, and it is a tremendous quality . . ." For these reasons he has frequently been spoken of as a 'live wire' by several distinguished personalities.

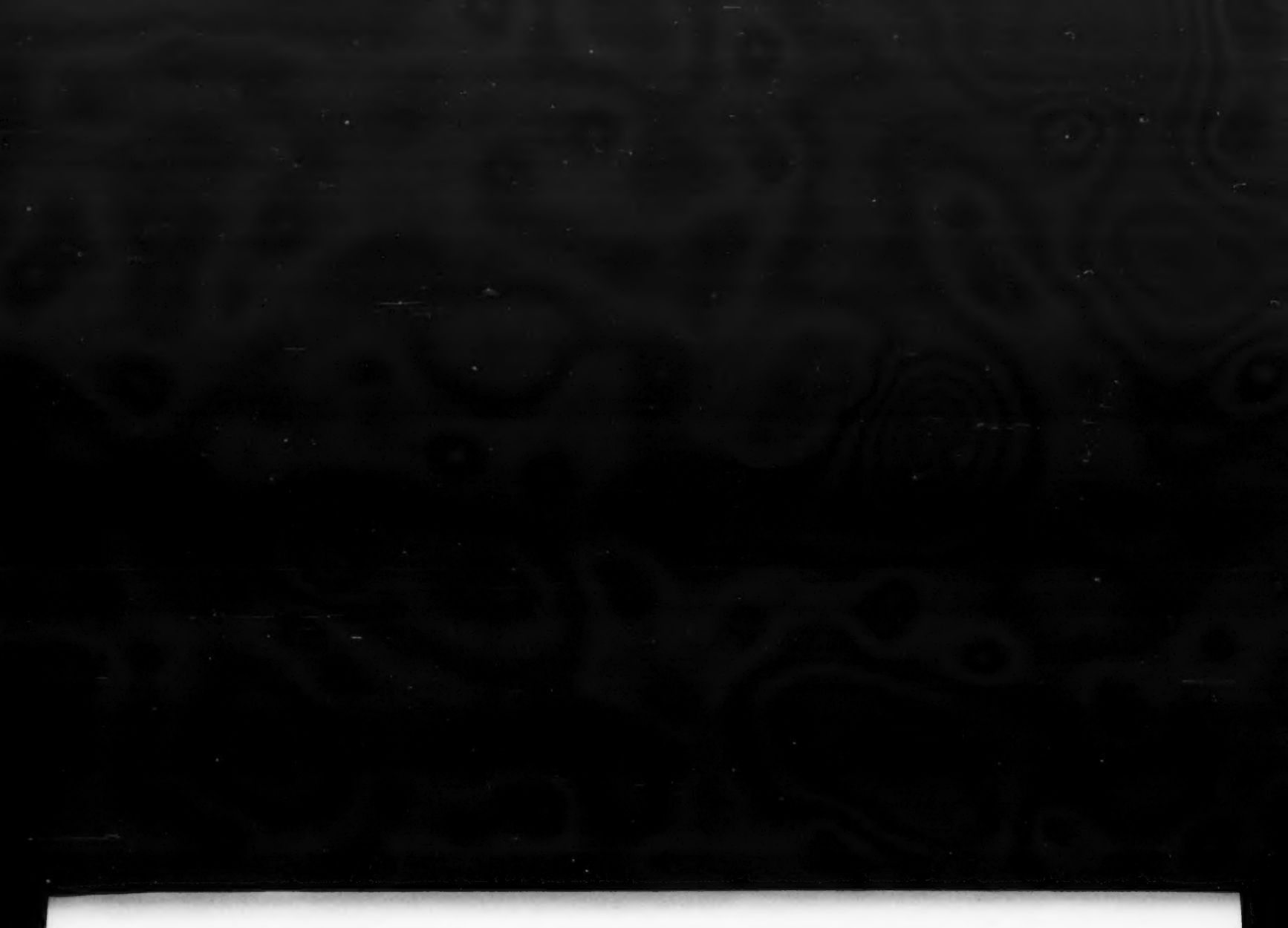
Dr. Bhatnagar was noble-minded and had a generous and affectionate heart for all persons, more so for his pupils, associates and fellow-workers. Visitors to his home were always treated very courteously and with the traditional Indian hospitality. Being himself an Urdu poet he would very often recite to them some of his own compositions, and make their stay with him enjoyable. Dr. Bhatnagar is a glorious instance of a self-made man. He knew well the financial difficulties which face keen research

workers, and hence gave away not only the large amount of money he received from M/s. Steel Bros., and as royalties from his patents but also a part of his salary for helping poor and well deserved young students. He had an acute sense of responsibility and, like Acharya P. C. Ray, for whom he had the greatest admiration, he always placed his duties and work foremost in life. He would be seen at work very early in the morning on all days, including Sundays and holidays, and would continue till late at night without rest ; he would seldom sleep for more than 3 to 4 hours.

The death of Dr. Bhatnagar is an irreparable loss not only to his friends and admirers, but to the national development and scientific progress of our country. It will be difficult to replace him with another person who has the same organising and administrative abilities and large-heartedness to sacrifice personal gains for the good of India which he loved so much. Let us strive to see that the new era of scientific activities which Dr. Bhatnagar founded so painstakingly may shine with glory by the selfless and notable contributions of scientific workers whom he leaves behind.

May his soul rest in peace.

M.P.



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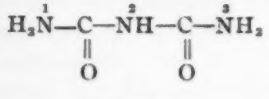
CHEMISTRY OF DICYANDIAMIDINES AND BIGUANIDES AND THEIR METALLIC COMPLEXES*

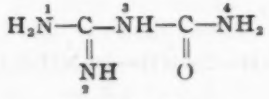
By Prof. Priyadaranjan Rây, M.A., F.N.I.

Chemically and structurally dicyandiamidine and biguanide are closely related to biuret; for, they may be viewed as derived from the substitution of one or both the oxygen atoms of the latter by the corresponding number of imino (=NH) groups:



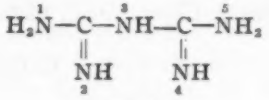
Biuret.

(I)



Dicyandiamidine.

(II)



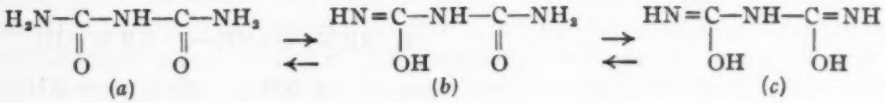
Biguanide.

(III)

Just as biuret is a condensation product of two molecules of urea, dicyandiamidine may be represented as derived from the condensation of one molecule of urea with one molecule of guanidine, and biguanide from the condensation of two molecules of guanidine. Their properties indicate that the substitution of each oxygen atom of biuret by an imino group progressively increases the basic character of the resulting product. Biguanide is a somewhat stronger base than dicyandiamidine, while biuret shows little basic character. This is in perfect agreement with the difference of basic properties between urea and guanidine. A consideration of the resonance energy of guanidine and guanidinium ion accounts for the strong basic character of guanidine.

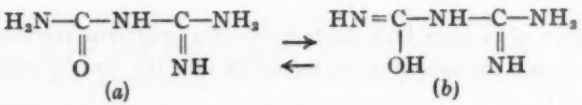
Biuret and dicyandiamidine can occur in two or more tautomeric forms, as represented below:

Biuret.



(a) (b) (c)

Dicyandiamidine.



(a) (b)

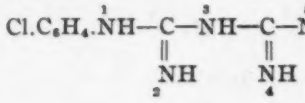
The biguanide molecule, and each of the tautomeric forms of biuret and dicyandiamidine can resonate among several valence bond structures. The number of

* Seventh Acharya P. C. Ray Memorial Lecture, delivered on August 2, 1954 in Calcutta.

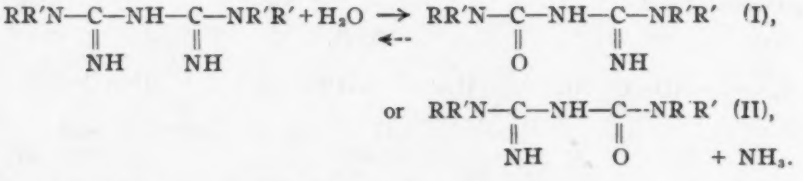
resonating structures for biuret will therefore be greater than those of dicyandiamidine, which latter again will be greater than those of biguanide.

Both dicyandiamidine and biguanide can form acid and normal salts. The first acid dissociation constant of biguanide is given by $pk_1 = 11.52$, whereas pk value for ammonia is 9.61. Biguanide is therefore a stronger base than ammonia and even stronger than diethylamine ($pk_1 = 10.96$). All the three compounds combine with metallic ions of the transitional group, yielding characteristically coloured co-ordinated chelate complexes of the inner-metallic type. We shall discuss these in some details hereafter.

One of the substituted biguanides, N^1-*para*-chlorophenyl-N^5-*iso*propylbiguanide, is now widely used as a valuable antimalarial under the name of *paludrine* (Curd and Rose, *J. Chem. Soc.*, 1946, 729).



A very interesting observation in respect of the chemistry of dicyandiamidine and biguanide was recently made in our laboratory dealing with the hydrolytic transformation of biguanide and substituted biguanides into the corresponding dicyandiamidines (Kundu and Rây, this *Journal*, 1952, **29**, 811). An acid solution of N^1-*p*-sulphonamidophenylbiguanide, on keeping overnight at the room temperature, was found to deposit wooly crystals of a corresponding dicyandiamidine salt. It was reported by Curd *et al.* (*J. Chem. Soc.*, 1949, 1732) that paludrine, when kept in aqueous hydrochloric acid for about one year, suffered transformation into a product, which separated out of the solution. This was identified and its constitution established by synthesis to be one of the two possible corresponding dicyandiamidines. For, a substituted biguanide may change by hydrolysis into two different but isomeric dicyandiamidines:



(where R = an aliphatic or aromatic hydrocarbon radical, and R′ = a hydrocarbon radical or H).

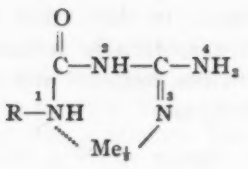
In the presence of an acid, HCl, for instance, the hydrolytic reaction would proceed leading to the complete conversion of the biguanide into the corresponding dicyandiamidine or guanylurea.

Curd and co-workers (*loc. cit.*) synthesised a number of such isomeric substituted dicyandiamidines and examined their antimalarial activity. For, they proceeded on the assumption that the specific action of paludrine against malarial organism might possibly be connected with the deamination *in vivo* of paludrine to yield the

corresponding dicyandiamidine. In fact, they found that some of the amidines, synthesised by them, showed appreciable antimalarial activities, but at the same time they observed that these activities, compared with those of biguanides, were much too small to support such an assumption.

The rapid hydrolytic change of N^1-*p*-sulphonamidophenylbiguanide in acid solution persuaded us therefore to pursue the matter further in this direction. The composition of the product of hydrolysis in this case, as determined by analysis, suggested that it might be one or the other isomeric dicyandiamidine or guanylurea, as discussed above, with the characteristic CO-group adjacent to the N^1- or N^4-nitrogen atom. In the former case, it will also be adjacent to the substituent sulphonamidophenyl group. In order to establish the identity of our product, we had to synthesise both the isomeric forms for comparison. But as the methods described by Curd and co-workers for the synthesis of isomeric amidines failed in this particular case, we had to develop entirely new methods for the purpose. I need not go into the details of these methods here. But one highly interesting observation that we made, while studying the properties of the two isomeric dicyandiamidines, is related to the great difference in their reactions towards copper and nickel salts in alkaline solution. While the one form with the carbonyl adjacent to the N^4- nitrogen atom and away from the *p*-sulphonamidophenyl group (structure II) yielded the characteristic coloured complex with copper and nickel salts, the other isomeric form (structure I) with the carbonyl adjacent to the *p*-sulphonamidophenyl group, altogether failed to react under the same conditions. This served to provide a very characteristic distinguishing test for the two isomeric forms. With a view to investigating the general applicability of this distinguishing test we prepared a variety of dicyandiamidines with substituents in N^1- and N^4- positions. As a result of this examination we have arrived at the general conclusion that all those substituted dicyandiamidines which contain phenyl group adjacent to its carbonyl fail to give characteristic copper and nickel complexes, while those with the carbonyl group adjacent to an alkyl substituent or unsubstituted N-atom yield as usual the characteristic coloured complexes. Phenyl, *p*-chlorophenyl, *p*-acetylphenyl, N^1-phenyl-N^4-pheuyl, N^1-phenyl-N^4-diethyl, N^1-*p*-sulphonamidophenyl, and N^1-*p*-sulphonamidophenyl-N^4-diethyl dicyandiamidines with the CO-group adjacent to the phenyl group, all failed to give any complex compounds with copper and nickel salts. On the other hand, the unsubstituted simple dicyandiamidine, the alkyl dicyandiamidines, N^1-phenyl-N^4-diethyldicyandiamidine with the CO-group adjacent to the N^4-atom, all gave the usual and characteristically coloured complexes with copper and nickel salts. It can therefore be concluded that the complex formation by dicyandiamidines is completely inhibited by the presence of an aryl group adjacent to the CO-group in the molecule.

A possible explanation of this behaviour can be offered as follows. The structure of the metallic complexes of dicyandiamidines might reasonably be assumed to be similar to that of the biguanide complexes and represented as follows:



In a structure of this type, the co-ordinating capacity of the N^1-atom will obviously depend on the nature of the substituent group R. If R be a negative or electrophyllic group like an aryl or substituted aryl group, characterised by the presence of double bonds, the co-ordinating capacity of the N^1-atom between the two electrophyllic groups, namely the aryl and the carbonyl, will obviously be reduced to a considerable extent. The carbonyl group containing a double-bonded oxygen atom, as well as the aryl group, with conjugated double bonds, will both tend to attract electrons from the N^1-atom, rendering it somewhat positive, thereby reducing its electrodotive or what is the same thing as its co-ordinating character.

A further point of interest arises from the observation of Curd and co-workers that while N^1-*p*-chlorophenyl-N^4-*iso*propylguanylurea (*i.e.* a substituted dicyandiamidine with CO-group adjacent to the aryl radical) shows some antimalarial activity, its isomeric dicyandiamidine, N^1-*p*-chlorophenylguanyl-N^4-*iso*propylurea, is devoid of any such activity. Similarly, they observed an antimalarial activity in the case of all the other N^1-*p*-chlorophenyl -N^4-alkyl- or -dialkylguanylureas This shows that there is a close relationship between the antimalarial activity and the position of carbonyl (-CO) group in the molecules of N^1-*p*-chlorophenyldicyandiamidine or guanylureas. This runs more or less antiparallel to their complex forming capacity as discussed above. All the active N^1-*p*-chlorophenyldicyandiamidines are characterised by having a carbonyl group adjacent to the aryl group and fail to react with copper and nickel salts to yield the corresponding complexes. This association of antimalarial activity of a compound with its incapacity for complex formation is of special significance in connection with the theories relating to the mechanism of the physiological activity of drugs.

The fact that N^1-*p*-sulphonamidophenylbiguanide was more or less completely changed in acid solution by deamination to the corresponding dicyandiamidine or guanylurea in 12 to 15 hours, while paludrine or N^1-*p*-chlorophenyl-N^5-*iso*propylbiguanide required about one year for such transformation to occur, at once suggested an enquiry into the effect of substitution on the rate of transformation of biguanides into guanylureas. Various substituted biguanides, for example, phenyl-, *p*-chlorophenyl-, *p*-sulphonic acid phenyl-, *p*-oxyphenyl-, ethyl-, diethyl-biguanides, etc., in presence of 2.5 *N*- HCl gave no such changed product in any appreciable amount in a month's time. An acid solution of phenylbiguanide deposited the product after a year, like paludrine. But rapid hydrolysis similar to that of N^1-*p*-sulphonamidophenylbiguanide had also been observed in the case of some of its derivatives, while in others the change was considerably retarded. This is evident from the following table.

TABLE I

p-$R^1R^2N.SO_2.C_6H_4.NH\text{-}C(:NH)\text{-}NH\text{-}C(:NH)\text{-}NR^3R^4$.

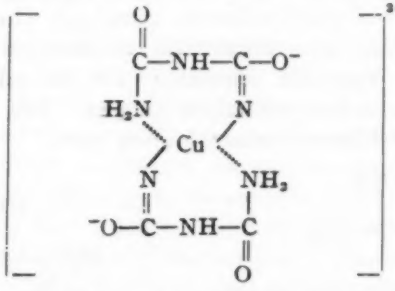
R^1.	R^2.	R_3.	R^4.	Observation in 2.5 *N*-HCl. $K_{46} \times 10^7$/-ec.	
H	H	H	H	Rapid change (within 15 hrs.)	28.00
C_2H_5	C_2H_5	H	H	,, ,,	38 40
CH_3	CH_3	H	H	,, ,,	39.70
CH_3	H	H	H	,, ,,	39.90
C_2H_5	H	H	H	,, ,,	39.70
C_6H_5	H	H	H	,, ,,	49 30
H	H	H	C_2H_5	Slow change	2 39
H	H	C_2H_5	C_2H_5	,,	1.76
H	H	H	C_6H_5	Change retarded (no appreciable change in one month)	
H	H	H	C_3H_7 (*iso*)	,, ,,	
C_2H_5	C_2H_5	H	C_6H_5	,, ,,	
C_6H_5	H	H	C_6H_5	,, ,,	
CH_3	CH_3	H	C_6H_5	,, ,,	
C_7H_5	H	H	C_6H_5	,, ,,	

K_{46} = specific reaction rate of the change at 46° (Kundu, this *Journal*, 1953, **30**, 627).

It may be noted that the presence of a sulphonamido group, $-SO_2NH_2$, in the *para* position of the phenyl group is essential for the rapid hydrolytic change or deamination of the biguanide. Substitution of one or both the hydrogen atoms of the sulphonamido group by an alkyl or aryl group shows very little effect on the rate of change. But the transformation is more or less inhibited by the substitution of one or more alkyl or aryl radicals in the N^5-position of the biguanide. This stabilising effect probably arises from increased resonance resulting from conjugation in the case of aryl and hyper-conjugation in the case of alkyl substituent in the N^5-position.

I shall now proceed to discuss the chemistry and the structure of the metallic complexes of biguanides and dicyandiamidines.

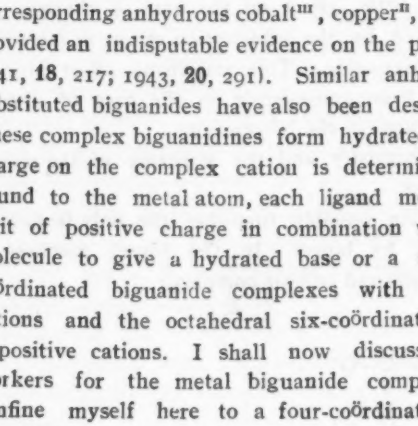
The long-known familiar biuret reaction possibly furnishes the only instance of the formation of such a metallic complex by biuret. In the biuret reaction the metallic copper atom forms the centre of a violet-red anionic complex :



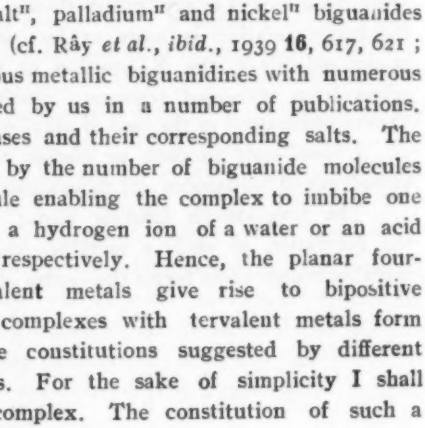
The constitution of the complex, as given above, is due to Ley and Wernet (*Ber.*, 1913, **46**, 4040).

But biguanide and its substituted derivatives have been found to give rise to numerous complexes with many bivalent and tervalent metals of the transitional series. These are all characterised by brilliant colours. Complex compounds of biguanides with Cu^{II}, and Ni^{II}, have long been described (Rathke, *Ber.*, 1879, **12**, 779, Emich, *Monatsh.*, 1883, **4**, 408; Smolka and Friedrich, *ibid.*, 1888, **9**, 227). As

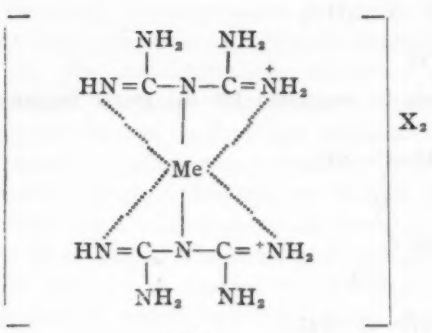
biguanides form cationic complexes, they have been obtained in the form of both free bases and their salts. There was, however, a considerable difference of opinion regarding the constitution of these complexes. A systematic investigation on the preparation and properties of these complexes containing not only the bivalent metals like copper and nickel, but also of those with bivalent cobalt, bivalent palladium, tervalent chromium, tervalent cobalt, tervalent silver, etc., carried out in our laboratory for the last sixteen—seventeen years, has revealed many interesting facts and led to many illuminating conclusions on the problems of valency and the structure of chemical compounds. We are now in a position to assign a more or less satisfactory constitution to the biguanide metal complexes. The bivalent metals as usual combine with two molecules of biguanide to form four-coördinated planar complexes, while the tervalent cobalt and chromium combine with three molecules of the ligand to produce six-coördinated octahedral configurations. The only exception is the tervalent silver which yields, however, a four-coördinated planar complex. The biguanide molecule behaves as a bidentate chelating ligand, giving rise to complexes of the inner-metallic type satisfying a primary as well as a secondary valency of the central metal atom. The preparation of the free chromium biguanide Cr $(C_2N_5H_6)_3$ in the anhydrous state (Rây and Sahu, this *Journal*, 1937, **14**, 670), as well as of the corresponding anhydrous cobalt^{III}, copper^{II}, cobalt^{II}, palladium^{II} and nickel^{II} biguanides provided an indisputable evidence on the point (cf. Rây *et al.*, *ibid.*, 1939 **16**, 617, 621 ; 1941, **18**, 217; 1943, **20**, 291). Similar anhydrous metallic biguanidines with numerous substituted biguanides have also been described by us in a number of publications. These complex biguanidines form hydrated bases and their corresponding salts. The charge on the complex cation is determined by the number of biguanide molecules bound to the metal atom, each ligand molecule enabling the complex to imbibe one unit of positive charge in combination with a hydrogen ion of a water or an acid molecule to give a hydrated base or a salt respectively. Hence, the planar four-coördinated biguanide complexes with bivalent metals give rise to bipositive cations and the octahedral six-coördinated complexes with tervalent metals form tripositive cations. I shall now discuss the constitutions suggested by different workers for the metal biguanide complexes. For the sake of simplicity I shall confine myself here to a four-coördinated complex. The constitution of such a complex, as suggested by different workers, is given below :



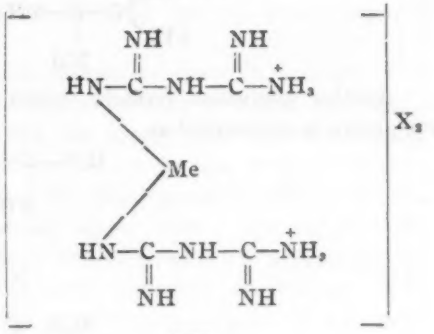
(I)



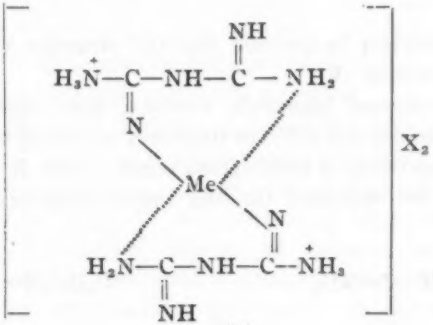
(II)



(III)



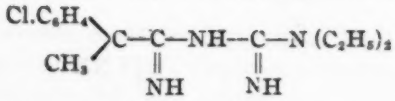
(IV)



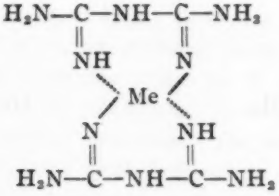
(V)

I—Tschugaef, *Ber.*, 1907, **40**, 1973.
II and III—Ley and Müller, *Ber.*, 1907, **40**, 2950.
III—Slotta and Tschesche, *Ber.*, 1929, **62**, 1390.
IV—Traube, *Ber.*, 1930, **63**, 2094. V—Rây and Sahu, *loc. c t.*

The fact that each biguanide molecule can occupy only two co-ordination positions, disposes of the constitutions (II) and (III) suggested by Ley and Müller, as well as by Slotta and Tschesche for the bivalent copper and nickel complexes, in which each biguanide molecule is made to function as tridentate ligand whereby a bipositive metal atom exhibits a maximum co-ordination number of six. In formula (III), there being four free amino groups, the complex should behave as a quadrivalent cation, which is not the case. Besides, formulla (III) is electronically impossible. Formu'a (IV), due to Traube, does not take any note of the co-ordination valency of the metal atom. Formula (I), due to Tschugaef, does not represent the complex as an inner-metallic salt which has been proved by the preparation of anhydro-metalbiguanidine bases. In formula (V), suggested by us, it has been shown that in the inner-metallic complexes formed by biguanide, it is the hydrogen atom of one of the imino groups (=NH) of biguanide, which is replaced by the metal atom to form a primary valence bond. This is supported by the formation of the coloured copper complex of N^1-*p*-chlorophenyl-N^1-methyl-N^5 : N^5-diethylbiguanide (cf. Curd and Rose, *J. Chem. Soc.*, 1946, 735):



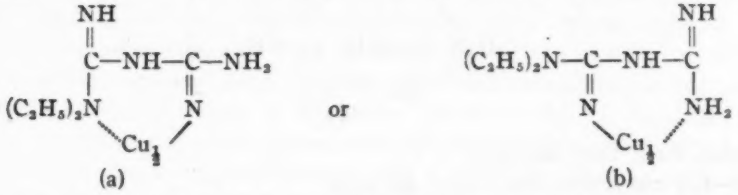
Another alternative formula, which may be suggested for the metal biguanide complexes, is represented as



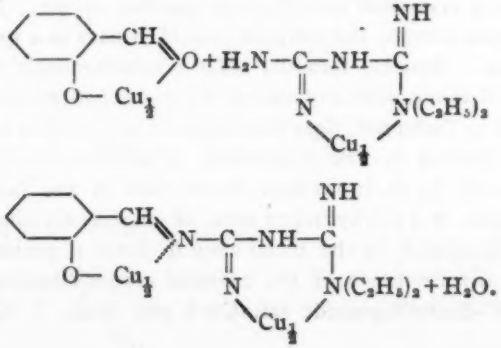
This would, however, make the complex behave as a quadrivalent cation or tetra-acidic base.

Hence, it may reasonably be assumed that the structure of biguanide complexes is best represented by formula (V).

In the case of a substituted biguanide, however, there again arises the question of deciding between the two possible different structures of a metal-biguanide complex, due to a difference in the disposition of metal-ligand bonds. This is evident from the following representation of the structure for the copper-diethylbiguanide, for instance:



A decision on this point was arrived at by treating a methyl alcoholic solution of the complex with a solution of copper salicylaldehyde in the same solvent, when a sand coloured crystalline product separated immediately (Rây and Ghosh, this *Journal*, 1949, **26**, 144). This indicated the presence of a free amino group in the copper diethylbiguanide complex, supporting the structure (a) for the complex. For, the reaction and the constitution of the product formed can only be represented as follows:



A binuclear, hetero-complex of copper is thus produced by the condensation of two copper complexes with different ligands.

As the metal-biguanide complexes usually behave as bases in solution, it is reasonable to assume that the more basic of the two amino or substituted amino-groups at the two ends of the biguanide ligand will remain free after the complex formation to combine with a hydrogen ion. In the present instance of copper diethyl-biguanide complex, therefore, the N-atom of the $-N(C_2H_5)_2$ group is utilised for the formation of a co-ordinate bond with the central copper atom. The fact that the bases and salts of the metallic complexes of N^1-dialkyl-substituted biguanides are rather unstable in aqueous solution and suffer rapid hydrolysis on heating, with separation of copper hydroxide, shows that the co ordinating capacity of biguanide is considerably weakened by such substitution. Similar instability has also been found in the case of metallic complexes of biguanide substituted at both N^1-and N^5-positions (Poddar and Rây, this *Journal*, 1952, **29**, 381). This provides an evidence in favour of the structure (a) for copper diethylbiguanidine as well as of the structure (V) proposed by us for the metal-biguanide complexes in general.

We have determined the acid dissociation constants of a number of biguanides and the instability constants of the corresponding copper complexes (Das Sarma and Rây, unpublished) with a view to exploring any relationship between the two. The first acid dissociation constant of biguanide and substituted biguanide is of the order of 10^{-12}, whereas the acid dissociation constant of ammonia is of the order of 10^{-10} approximately. The biguanides therefore are stronger bases than ammonia, and in this respect resemble the alkylamines, the values of whose acid dissociation constants lie between 10^{-12} and 10^{-10}.

The relative basic strengths of a number of biguanides can be represented by the following arrangement:

$$\underset{2.09}{N^1\text{-Diethylbiguanide}} > \underset{2.82}{\text{ethylenedibiguanide}} > \underset{3.02}{\text{biguanide}} =$$

$$\underset{3.02}{N^1\text{-dimethylbiguanide}} > \underset{3.39}{\text{ethylbiguanide}} > \underset{3.63}{\text{methylbiguanide}} >$$

$$\underset{19.1}{\text{phenylbiguanide}} > \underset{23.40}{m\text{-phenylenedibiguanide}} > \underset{57.5}{\alpha\text{-naphthylbiguanide}}$$

The numbers below the names give their first acid dissociation constant ($K_{a_1} \times 10^{12}$) values, except in the case of ethylenedibiguanide and *m*-phenylenedibiguanide where they represent $\sqrt{K_{a1} K_{a2}}$ values (average).

The relative stabilities of the corresponding copper complexes can also be arranged in a decreasing order as follows:

$$\underset{0.002}{\text{Cu-ethylenedibiguanide}} > \underset{4.54}{\text{Cu-biguanide}} > \underset{70.52}{\text{Cu-methylbiguanide}} >$$

$$\underset{101.9}{\text{Cu-ethylbiguanide}} > \underset{177.0}{\text{Cu-phenylbiguanide}} > \underset{36310\ 0}{\text{Cu-}m\text{-phenylenedib'guanide}} >$$

$$\text{Cu-}N^1\text{-diethylbiguanide} = \text{Cu-}N^1\text{-dimethylbiguanide}.$$

The numbers below the names give the values of their overall instability constant ($K_{Cu} \times 10^{19}$,.

The corresponding nickel complexes, however, show the following order of their stability :

Ni-ethylenedibiguanide > Ni-biguanide > Ni-methylbiguanide =
0.708 3.31 166.0

Ni-ethylbiguanide > Ni-phenylbiguanide
166.3 424.8

The numbers here give values for $K_{Ni} \times 10^{14}$.

The order of stability of the complexes with different biguanides remains more or less the same for both copper and nickel, but a copper complex is much more stable (about 10^5—10^6 times) than the corresponding nickel complex.

From a comparison of the relative basic strengths of the biguanides with the relative stabilities of their copper or nickel complexes, it will be observed that there is no simple relationship between the two.

The study of the instability constants of the copper and nickel biguanide complexes has further revealed that while the copper biguanide complexes suffer stepwise decomposition with the formation of an intermediate monobiguanide complex, the nickel complexes decompose in a single stage. Guided by this observation, we succeeded in preparing a number copper monobiguanide complexes, $[Cu(BigH)]X_2$, where BigH is a biguanide molecule, simple or substituted. (Das Sarma and Rây, this *Journal*, 1951, **28**, 347).

Measurement of the instability constant of biguanide complexes with the tervalent metals like cobalt and chromium shows that the cobalt complexes are more stable than the corresponding chromium complexes, and that the simple biguanide complexes are more stable than their phenylbiguanide analogues (De, Ghosh and Rây, this *Journal*, 1950, **27**, 493; Bandopadhyaya, Ghosh and Rây, *ibid.*, 1952, **29**, 865). The overall instability constant values for the cobaltic complexes are of the order of 10^{-50} to 10^{-55} and that for the chromium complexes is somewhat less.

The use of a substituted biguanide, ethylenedibiguanide, as a co-ordinating ligand has enabled us to stabilise a higher valency (tervalency) state of silver by the preparation of the tri-positive silver complex in the form of its hydroxide, sulphate, nitrate and perchlorate, $Ag[Et(BigH)_2]X_3$, where $Et(BigH)_2$ = one molecule of ethylenedibiguanide, $X = OH^-$, $\frac{1}{2}SO_4^{2-}$, NO_3^- or ClO_4^- (Rây and Chackravarty, *ibid.*, 1944, **21**, 47). These compounds are diamagnetic as might be expected from theoretical consideration, while the bipositive silver complexes are paramagnetic. The complex nitrate forms dark red needle-shaped crystals, difficultly soluble in dilute nitric acid. The compound is quite stable and does not suffer any appreciable change even in boiling aqueous nitric acid solution. A quantitative study of the equilibrium constant of the reaction between silver complex and hydrogen ion and of the acid dissociation constant of the base gave the instability constant for the complex ion to be of the order 10^{-52} (Sen, Ghosh and Rây, *ibid.*, 1950, **27** 619), which is comparable with that of cobaltic *tris*biguanide complex (10^{-55}) and considerably higher than that of cobaltammines (10^{-34}). This represents a very high degree of stability, and the complex is about

10^{18} times more stable than the cobaltammine complexes. Nevertheless, it is found to decompose slowly in aqueous solution on keeping. The velocity of its decomposition has been found to follow more less the law of unimolecular reaction (Sen and Rây, *ibid.*, 1953, **30**, 519). The decomposition is attributed to the reduction of the tervalent silver ion, Ag^{3+}, in water according to the side reaction:

$$Ag^{3+} + H_2O \rightleftarrows Ag^{+} + 2H^{\bullet} + \tfrac{1}{2}\,O_2.$$

This disturbs the equilibrium dissociation of the complex,

$$[Ag\ (Et\ BigH)_2]^{3+} \rightleftarrows Ag^{3+} + Et\ (BigH)_2,$$

leading ultimately to its complete decomposition.

From a consideration of the instability constants of metal biguanide complexes the co-ordinating capacity of different metal ions can be arranged in the following order:

$$\underset{10^{-55}}{Co^{III}} > \underset{-}{Cr^{III}} > \underset{10^{-19}}{Cu^{II}} > \underset{10^{-14}}{Ni^{II}}.$$

The figures below give the approximate overall instability constants of their biguanide complexes. The overall value for Cr^{III} could not be determined. But a consideration of its first two instability constants (K_3 and K_2) values places it immediately after cobalt^{III}.

Some copper biguanide complexes have been obtained in two differently coloured crystalline modifications. These are copper-diethylbiguanide (red and blue violet), copper *p*-sulphonic acid phenylbiguanide (green and red), copper-phenylbiguanide (light pink and dark red) and its corresponding chloride (blue violet and red) (Rây *et al.*, this *Journal*, 1941, **18**, 609; 1949, **26**, 144; 1943, **20**, 250; 1948, **25**, 563). In aqueous, alcoholic, or pyridine solution both the modifications of one and the same complex give, however, identical absorption and identical colour. So, it is not easy to distinguish whether the colour difference arises from an actual difference in their molecular configuarations giving *cis-trans* arrangement, or merely from a difference in the particle size or crystalline structure (polymorphism). We have recently been able to obtain through the courtesy of Sadtler Research Laboratories, Philadelphia, U. S. A, infra-red absorption spectra for the solid crystals of some of these compounds, which decisively indicate a difference in the molecular structure for each pair (Figs. 1-4). This suggests that the two modifications are related to each other as *cis-trans* isomers. But as both the varieties give identical colour and absorption in aqueous, alcoholic, or pyridine solution, one of them (probably *cis-*) must be extremely unstable in solution, changing rapidly into the more stable form. Planar structure for some typical four-coördinated copper (II) complexes has been revealed by their X-ray examination, though till now there is no evidence regarding the occurrrence of *cis-trans* isomers among such complexes. The above described copper biguanide complexes, as indicated by their infra-red absorption spectra, possibly provide the first instances of such isomerism in four-coördinated copper complexes, though occurring only in the crystalline state.

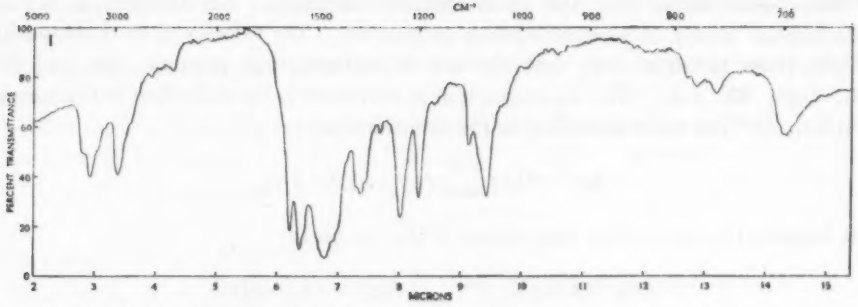


Fig. 1. Copper diethylbiguanide (blue) : $C_{12}H_{28}CuN_{10}$.
Mol.wt. 375.99; 1.9 mg. in 190 mg. KBr. 0 46 mm.
Peaks at: 2.95, 3.4, 6 2, 6.38, 6 76, 7.38, 8 0, 8 3 9.42, 13 2 and 14 3 μ.

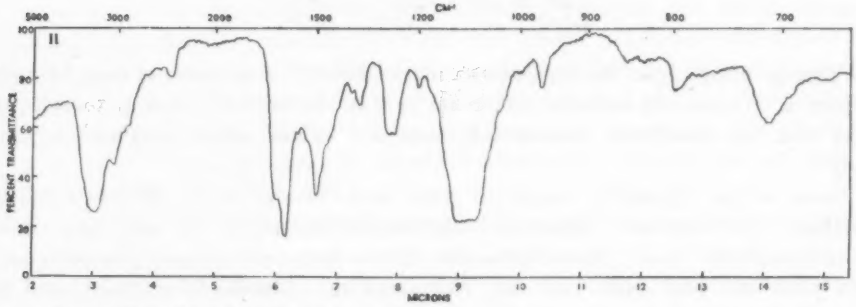


Fig. 2. Copper diethylbiganide (red): $C_{12}H_{28}CuN_{10}$.
Mol.wt. 375.99. 1.6 mg in 160 mg. KBr. 0.35 mm
Peaks at: 3.0, 3.38, 6.0, 6.18, 6.7, 7.4, 7 9, 8.3, 9.2, 10 38, 12 58, 14.10 μ.

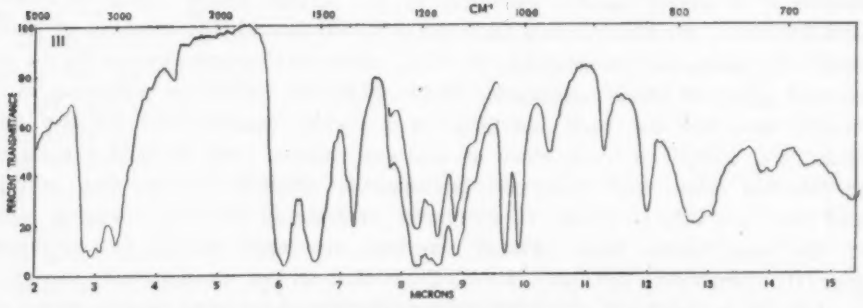


Fig. 3 Copper *p* sulphonic acid phenylbiguanide (green): $C_{16}H_{20}CuN_{10}O_6S_2$, $5H_2O$ (*Cis*).
Mol wt. 666.18; 2.2 mg in 220 mg KBr, 0.49 mm.
Peaks at: 2.8, 3.28, 4 3, 6.1. 6.6, 7 2, 8.24, 8 6, 8.84, 9.64, 9.9, 10.4, 11.3, 12.0, 12.7, 13.1, 13.82, 14.0, 15.18 μ.

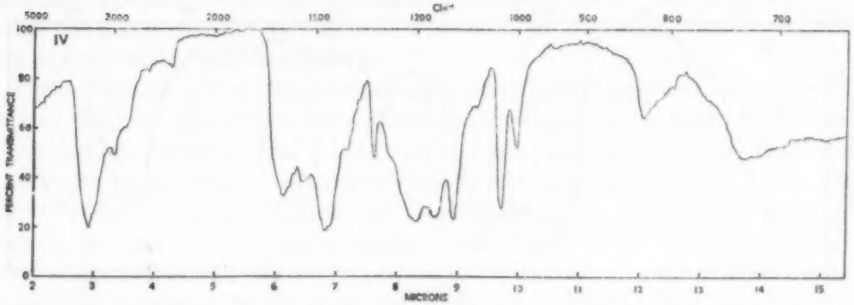


Fig 4. Copper *p*-sulphonic acid phenylbiguanide (red-violet): $C_{16}H_{20}CuN_{10}O_6S_2$, $5H_2O$. *Trans*).
Mol. wt. 666 18; 1 9 mg. in 190 mg. KBr, 0.44 mm
Peaks at: 2.9, 3.28, 4.3, 6.1, 6.4, 6.8, 7.6, 8.3, 8.6, 8.9, 9 7, 9 9, 12.1, 13 7 μ.

Three modifications of nickel phenylbiguanide, differing in their colour—red, light yellow and deep yellow—were obtained (Rây and Chakravarty, *ibid.*, 19;1, **18**, 609). The last one, as the infra-red spectrogram shows, is identical with the second one and the first two are possibly related as *cis-trans* isomers to each other (Figs. 5-7).

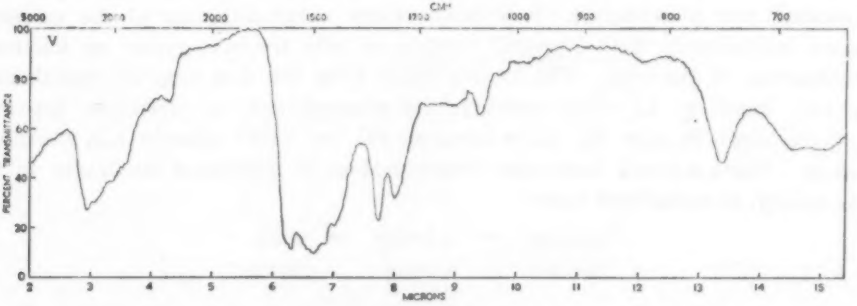
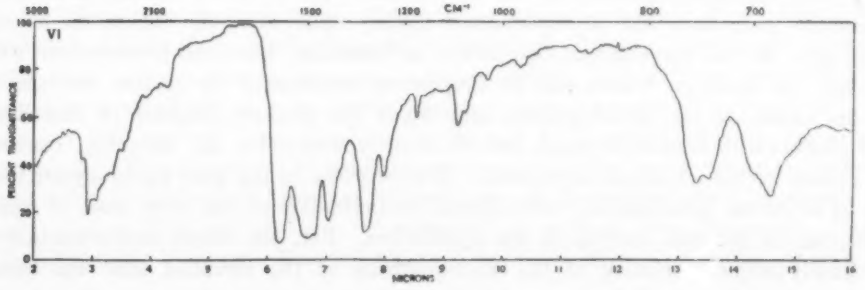


Fig. 5. Nickel phenylbiguanide (red): $C_{16}H_{20}N_{10}Ni$. (*Trans*).
Mol. wt. 411.09; 2.5 mg in 250 mg. KBr, 0.56 mm
Peaks at: 2.9, 4.3, 6.3, 6.68, 7.0, 7.7, 8.0, 9 4, 12.0, 13.28 μ.



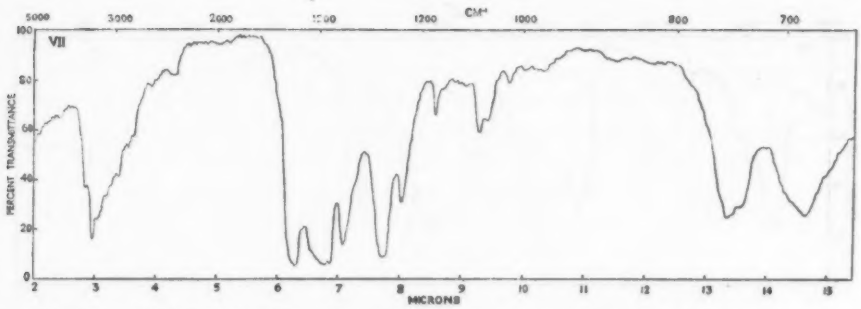


Fig. 6 and Fig.7. Nickel phehylbiguanide (light and deep yellow) : $C_{16}H_{20}N_{10}Ni$. (*Cis*).
Mol. wt. 411.09; 1 8 mg. in 180 mg. KBr. 0.41 mm.
Peaks at :2.95, 4.3, 6.3, 6.7, 7.08, 7.7, 8.0, 8.38, 9.3 9 78, 10.0, 12,0, 13 3, 14.6 μ.

The form showing a larger number of absorption peaks possibly represents the *cis*-configuration, as some of the vibrations become forbidden in the case of the *trans* form due to its symmetry.

The resolution of the cobaltic *tris*biguanidinium chloride into its optically active enantiomerides (Rây and Dutt, *ibid.*, 1941,**18**, 1941, 289) has revealed an instance of the interesting phenomenon of asymmetric transformation of the second order as described by Kuhn. This is possibly the first example of an inorganic complex salt manifesting this phenomenon. A solution of the chloro-*d*-tartrate of the racemoid cobaltic *tris*biguanide base deposited crystals of only the *laevo*-gyrate on fractional crystallisation in the cold. The mother-liquor from the first crop of crystals was, however, found to be *dextro*-rotatory, but when allowed to crystallise, deposited successive crops of only the *laevo*-isomeride till the entire solution was practically dried up. There is thus a continuous transformation in solution of the *dextro* to the *laevo*-variety, as represented below :

Solution	→	solution	→	solid
(*dextro*)		(*laevo*)		(*laevo*)

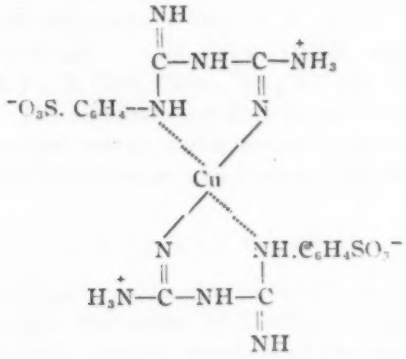
Both the diastereoisomerides are formed in equal quantities in solution to begin with and tend to approach an equilibrium as they are mutually convertible, but before the kinetic equilibrium is established, the less soluble *laevo*-salt separates out from the solution.

The chloro-*dextro*-tartrate of the *dextro*-base was, however, obtained in the pure crystalline state from the *dextro*-rotatory mother-liquor, after the separation of the first crop of the *laevo*-diastereoiso neride, by immediate fractional precipitation with alcohol. It therefore follows that the equilibrium condition of the system corresponds to an exesss of the *dextro*-gyrate, and hence the product obtained by immediate precipitation with alcohol, in which both the diastereoisomerides are insoluble, contains an excess of the complex *dextro*-salt. The isolation of the pure *dextro*-gyrate from this by fractional precipitation with alcohol is indicative of the slow rate of transformation in solution leading to an equilibrium. For, the slight *dextro*-rotation of the freshly prepared solution of the *dextro*-tartrate of the racemoid base was found

to increase gradually with time to a constant maximum value. The same equilibrium rotation was also arrived at, starting from a solution of the *laevo*-rotatory as well as of the *dextro*-rotatory diastereoisomeride.

From the two active diastereoisomerides pure *dextro*- and *laevo*-isomerides of the chloride, sulphate and nitrate of the cobaltic *tris*biguanide complex were obtained with molecular rotations, $[M_D^{31}]$, of $\pm 2100°$, a value considerably higher than that of the optically active cobaltic *tris*ethylenediamine complex salts ($\pm 600°$). The higher rotation of the *tris*biguanidinium ion is indicative of its lower degree of symmetry compared to that of *tris*ethylenediamine-cobaltic ion. This furnishes an indirect evidence and support of the unsymmetrical co-ordination of the symmetrical biguanide molecules, as suggested by us (Ray and Sahu, *loc. cit.*). In fact, phenylbiguanide being itself an unsymmetrical molecule gives an active cobaltic *tris*phenylbiguanide ion having a molecular rotation, $[M_D^{31}]$, of $\pm 2500°$ higher than that of even cobaltic-*tris*biguanide ion.

A substituted biguanide like *p*-sulphonic acid phenyl- and *o*-sulphonic acid naphthyl-biguanide can give rise to ampholytic inner-metallic complexes, which are non-electrolytes and insoluble in water. But they dissolve in both acids and alkalies. With alkalies they give well-defined crystals of the corresponding alkali salts. These ampholytic complexes have therefore been termed as inner-metallic complexes of the fourth order (Rây and Datta, this *Journal*, 1948, **25**, 563). *Eg.*:



A short account of the metallic complexes of dicyandiamidine or guanylurea will now be given here. It has already been stated, that as a complexing agent, dicyandiamidine is much inferior to biguanide, though stronger than biuret. This probably follows from their molecular constitution. Being a tautomeric molecule, with each tautomeric form resonating among several valence bond structures, the molecule is stabilised to a somewhat greater extent than the biguanide molecule, and hence, is less reactive than the latter so far as its complex forming capacity is concerned. This difference is much more pronounced in biuret which can occur in three different tautomeric forms as against two of dicyandiamidine. Moreover, the basic character of the molecule decreases as we proceed from biguanide through dicyandiamidine to biuret. For, it is generally found that the co-ordinating capacity of a

ligand diminishes or even vanishes, if its electrodotic or basic character exceeds or falls below a certain optimum range. Too strong a base tends to form an ionic compound by combining with hydrogen ion, and too weak a base with little tendency for donating electrons fails to co-ordinate. A study of the preparation and properties of the complex compounds of dicyandiamidine and its phenyl derivative with copper, nickel, cobalt (III) and palladium (Rây and Bandopadhyay, this *Journal*, 1952, **29**, 865) supports this view. Most of these complexes are unstable even to warm dilute alkalies.

The constitution of metal dicyandiamidine complexes is best represented by a configuration similar to that of biguanide complexes, as the complex bases of the two series have got similar colour, viz., copper—violet-red, nickle and palladium—yellow to orange-yellow, and cobalt (III)—dark-red. The constitution of these complexes has been depicted before.

We thus find that a study of the preparation and properties of metal biguanide and metal-dicyandiamidine complexes has revealed many new facts and phenomena of considerable significance to the co-ordination and structural chemistry.

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THE PHASE-DIAGRAM STUDY OF THE SYSTEM NAPHTHALENE-SALOL

By D. K. Majumdar and P. C. Rakshit

The phase-diagram of the binary system of naphthalene-salol has been studied. The *t-c* curve suggests the formation of a simple eutectic and no chemical union appears to take place. The eutectic melts at 25.49° with a composition of 22% naphthalene by weight.

The mixture of salol and various other solids readily begins to liquefy even at ordinary temperatures. It would be worthwhile to investigate if any chemical change is involved in such transformation. The present communication deals with the binary system of naphthalene and salol, studied from the point of view of freezing points of different compositions.

There are some observations in this line about naphthalene in the literature. In phase diagram studies, *m*-dinitrobenzene (Skau, *J. Amer. Chem. Soc.*, 1930, **52**, 945) and other polynitro-aromatic compounds, e.g., 1 : 2:4:6 tetranitrobenzene, 2 : 4 : 6-trinitroethoxy- or trinitrobenzene (Shinomiya, *Bull. Chem. Soc., Japan*, 1940, **15**, 92, 137) show the formation of definite molecular compounds with naphthalene ; while diphenyl (Lee and Warner, *J. Amer.Chem. Soc.*, 1935, **57**, 318), *p*-dichlorobenzene (Morris and Cook, *ibid.*, 1935, **57**, 2403), hexachloroethane (Pariys, *Z. anorg. Chem.*, 1936, **226**, 425), phenanthrene (Klochko-Zhovnir, *J. Appl. Chem., USSR.*, 1949, **22**, 848), *p*-nitrotoluene (Crockford and Simmons, Jr., *J. Phys. Chem.*, 1933, **37**, 259) etc. lead to the formation of simple eutectics only. Hrynakowskio and Szmytowne (*Arch. Parm.*, 1935, **273**, 163) investigated the salol-bromural system which formed a eutectic mixture. It was reported earlier that the salol-benzophenone (this *Journal*, 1952, **29**, 196) system showed a simple eutectic.

Experimental

Known amounts of salol and naphthalene (chemical reagent varieties of B.D.H.) were taken in a large test tube, surrounded by a wider air-jacket. The tube was provided with a stopper carrying a sensitive standardised thermometer and a stirrer. The mixtures were completely melted by keeping the system in a water-bath and sufficient time was allowed to attain equilibrium. The two components were completely miscible in the liquid state. The tube was then transferred to a Dewar flask and allowed to cool slowly under a standard set of conditions with uniform mechanical stirring in each experiment. The time-temperature readings were taken during the process of cooling. The cooling curves of the mixtures showed two arrest-points corresponding to the liquidus and solidus respectively. The freezing points of the pure components were also determined by the same methods.

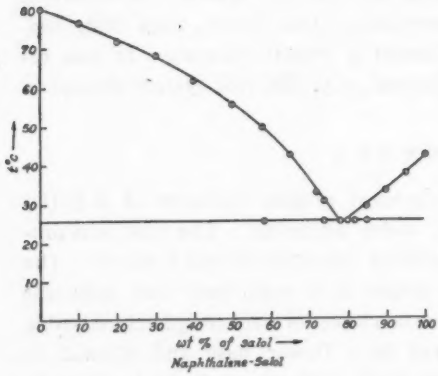
When the first arrest-points of the time-temperature cooling curves of the various compositions were plotted, the liquidus of the binary system was obtained. These data of freezing points are recorded in Table I and the corresponding plot shown in Fig. 1.

TABLE I

Wt.% of salol.	Freezing point. Initial.	Final.	2+log N.	$10^3/T$.	Wt % of salol.	Freezing point. Initial.	Final.	2+log N.	$10^3/T$.
100%	42.0°	42.0°	2.000	3.175	72 %	32.2°	...	1.5956	3.276
95	37.09°	...	1.9633	3.225	65	42.26°		1.6757	3.173
90	33.1°	...	1.9260	3.268	58.4	49.11°	25.4°°	1.7354	3.105
85	28.59°	25.49°	1.8877	3.316	50	55 38°		1.7963	3.046
82	...	25.49°	...	...	40	61.66°		1 8542	2.988
80	...	25.49°	...	...	30	67.94°		1.9009	2.934
78	25.49°	25.49°	1.8322	3.352	20	71.3°		1.9395	2.904
74	30.2°	25.49°	1.5683	3.298	10	76.59°		1 9720	2.862
					0	80.05°		2.000	2.832

In the temperature-composition graph there is one single point, which is a minimum and where the liquidus from either side meet the solidus. The system therefore admits of no chemical union but behaves as a simple eutectic. The eutectic point is 25.49° and the corresponding composition is 78% salol and 22% naphthalene by weight. The eutectic point was confirmed by taking a mixture of the above-mentioned composition which melted and froze at the same temperature as noted above. It has also been corroborated by the fact that the second arrest-points in time-temperature (cooling) curves correspond also to the same temperature of 25.49°. This latter fact also shows that the two components would not form a solid solution. Besides, the crystals separating in the initial stages of cooling on the right and left sides of the eutectic point were pure salol and naphthalene respectively, verified from melting points. The solid mixtures of different compositions also begin to melt at 25.49°, clearly proving the eutectic nature.

FIG. 1



Two separate curves obtained from time-temperature record during cooling of the melt (Figs. 2 & 3) illustrate the nature of the arrest points, and specially the super-

FIG. 2

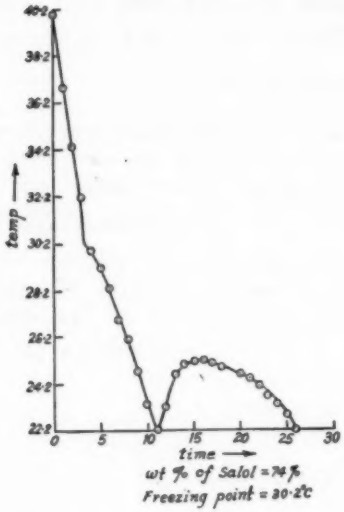
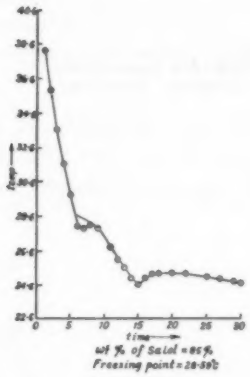


FIG. 3



cooling involved in the freezing. It is interesting to note that the cooling curves with higher percentage of naphthalene exhibit very little supercooling, whereas those with a higher percentage of salol have large supercooling depressions; obviously the crystal formation is handicapped due probably to viscosity reasons. This aspect is now under investigation.

Assuming

$$\triangle H_f = -2375 + 38.10T - 0.0528T^2$$

to be the molar latent heat of fusion of naphthalene (Lee *et al.*, *loc. cit.*), the mol. fraction N_1 of naphthalene can be expressed for an ideal binary system with the help of the Clausius-Clapeyron equation,

$$\ln N_1 = -\frac{\triangle H_f}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right).$$

Substituting N_1 from eutectic composition, the eutectic temperature T can be calculated. The plot of log N_1 against $1/T$ also should be linear. Similar values can also be obtained for the mol. fraction of salol. In the case of salol, the values of $\triangle H_f$ is only approximately calculated from the knowledge of molal freezing point constant (*Gazzetta*, 1904, **34**, 101),

$$\frac{0.002T^2}{L_f} = K_f = 12.3$$

denoting the latent heat of fusion in calories per gram. The values are shown below, and the plots of log N_1 (or log N_2) against T exhibit linear relationships.

TABLE II

Eutectic temperature.

Exp.	Calc. from ΔH_f for Naphthalene.	Salol.
25·49°	24·7°	21·5°

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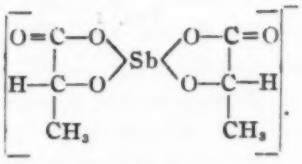
THE STUDY OF LACTATE COMPLEX OF TRIVALENT ANTIMONY BY GLASS ELECTRODE

By G. Patra and S. Pani

Lactate complex of trivalent antimony has been investigated by p_H titration method. Two complexes containing respectively one and two lactate ligands per antimony atom exist. The equilibrium constant of the reaction for the formation of the second complex containing two lactate ligands has been calculated.

Lactate complex of antimony was investigated by Mohanty and Pani (this *Journal*, 1954, **31**, 593) and they found a complex containing two lactate ligands per atom of antimony. It has been suggested that the lactate ligand behaves as a bidentate group and the complex is



(X)

There is, however, no direct evidence for the hydroxyl group to unite with the liberation of hydrogen ion, as proposed above, though it appears to be probable. This investigation was undertaken to study the system more thoroughly.

Experimental

Antimony chloride solution of the same quality and strength (0.0414 *M*) was employed as by Samontora *et al.* (this *issue*, p. 165). To 25 c.c. of this solution 250 c.c. of 0.4678*M* lactic acid solution and 87.5 c.c. of 0.9917 *N*-NaOH solution were added (the alkali was added to neutralise the free HCl in the solution). The p_H of the resulting solution was measured after adding increasing amounts of alkali (0.9917 *N*). There was no precipitation of antimony hydroxide. The experimental results are graphically shown in Fig. 1, curve A.

In another set of experiments 25 c.c. of 3.471*N*-HCl was mixed with 250 c.c. of 0.4678 *M* lactic acid and 87.5 c.c. of 0.9917 *N*-NaOH. The p_H of the resulting solution was measured after adding increasing amounts of 0.9917 *N*-NaOH as done before. The results obtained are graphically represented in curve B, Fig. 1.

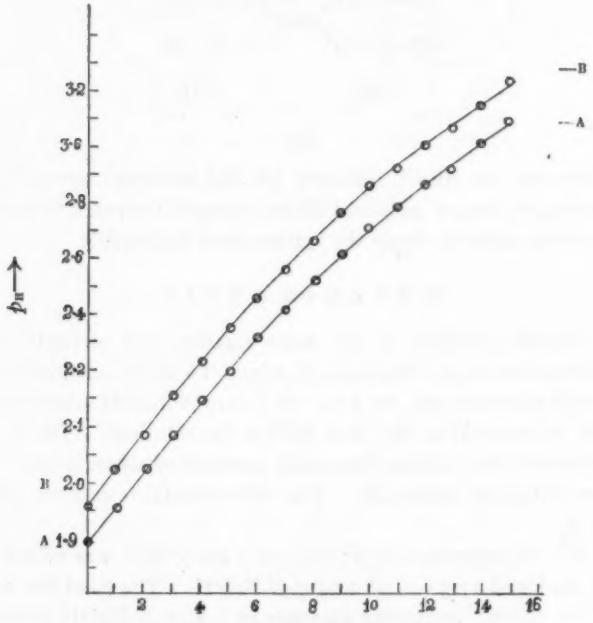
The large concentration of lactic acid compared to that of antimony chloride was maintained due to the following reasons. The formation of the lactate complex would be complete so that there would be no hydrolysis. The amount of the lactate present in the complex would be small and there would be no appreciable change in the concentration of lactic acid. Besides, the amount of hydrochloric acid liberated due to the

formation of the complex would be small and there would be no change in the nature of the neutralisation curve of lactic acid. This is evident from Fig. 1. The reaction can be represented by

$$SbCl_3 + nCH_3.CH(OH).COO^- \rightleftarrows \left[Sb\left(\begin{array}{c} O-C=O \\ | \\ O-CH \\ | \\ CH_3 \end{array} \right)_n \right]^{+3-2n} + 3\,Cl^- + nH^+ \quad \ldots \quad (1)$$

From the above equation it is evident that the number of the lactate ligands present in the complex is equal to the number of hydrogen ions liberated in the reaction. The p_H of the system containing antimony chloride is expected to be lower than that of the other system and has been actually observed. The horizontal distance between the two curves in Fig. 1 indicates the amount of alkali which should be added to the system containing antimony chloride so that both the systems would have the same p_H. It is therefore the amount of acid liberated due to the formation of the complex.

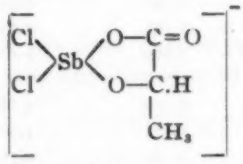
FIG. 1



From the very beginning the horizontal distance between the two curves indicates that one equivalent of acid per atom of antimony has been liberated. Therefore the complex, Sb_1, contains one lactate ligand per atom of antimony and the hydroxyl group is attached to the antimony atom with the liberation of hydrogen ion. With the rise of p_H the horizontal distance between the two curves progressively increases, and hence, the

amount of acid liberated becomes more than one equivalent per atom of antimony. At p_H 2.6, the amount of acid liberated becomes two equivalents per atom of antimony. The complex Sb_{II} at this p_H therefore contains two lactate ligands per atom of antimony. After this there is no change in the horizontal distance between the two curves. The complex formation therefore takes place in two steps.

The second complex is as shown in the beginning (X). It is therefore most probable that the co-ordination number in the first complex is also four and can be represented as :



(Y)

The reactions can be represented by

$$SbCl_3 + CH_3.CH(OH).COO^- \rightleftharpoons (Y)^- + Cl^- + H^+ \quad \ldots (2)$$

$$(Y)^- + CH_3.CH.(OH)\,COO^- \rightleftharpoons (X)^- + 2Cl^- + H^+ \quad \ldots (3)$$

It is not possible from the existing data to calculate the equilibrium constant of the reaction (2) since the formation of the first complex Sb_I is complete. The equilibrium constant of the reaction (3) is given by equation (4) where $[Sb_I]$, $[Sb_{II}]$, $[La^-]$, $[H^+]$ and $[Cl^-]$ represent the molar concentration of the first complex, the second complex, lactate ion, hydrogen ion and chloride ion respectively.

$$\frac{[Sb_{II}] \times [H^+] \times [Cl^-]^2}{[Sb_I]\,[La^-]} = K_2. \quad \ldots \quad \ldots (4)$$

Since the total concentration of chloride ion is very large compared to the total concentration of antimony in the solution, the liberatton of chloride ion due to the formation of the complex would change the concentration of the chloride ion to a very small extent. The concentration of chloride ion therefore can be taken as constant. Hence

$$\frac{[Sb_{II}]\,[H^+]}{[Sb_I]\,[La^-]} = K \quad \ldots \quad \ldots \quad \ldots (5)$$

$[Sb_I]$, $[Sb_{II}]$ and $[H^+]$ are obtained from the curve. Horizontal lines perpendicular to the p_H axis are drawn which cut the two curves. The distance between the two curves gives the amount of acid $[A]$ liberated due to the formation of the complex at the p_H represented by the point in the p_H axis, where the horizontal line meets. When the formation of the first complex is complete, $[A] = [Sb]$ where $[Sb]$ is the total antimony in the solution. When the formation of the second complex is complete, $[A] = 2\,[Sb]$. At any intermediate p_H.

$$[A] - [Sb] = [Sb_{II}] \quad \ldots (6)$$

and

$$[Sb_I] + [Sb_{II}] = [Sb] \quad \ldots (7)$$

$[Sb_I]$ and $[Sb_{II}]$ are calculated by equations (6) and (7). $[La^-]$ is calculated from the dissociation constant of lactic acid (1.82×10^{-4} ; Cannan and Kibrick, *J. Amer. Chem.*

Soc., 1938, **60**, 2314) and the p_H value obtained from the curve neglecting the amount of lactate ligand present in the complex, since it is very small compared to the total lactic acid originally taken. The results are shown in Table I. The mean value of K is 0.67.

TABLE I

p_H.	G. mols. of total Sb. in the soln. $\times 10^4$. $[Sb] \times 10^4$.	G. mols. of Sb_I in the soln $\times 10^4$. $[Sb_I] \times 10^4$.	G. mols. of Sb_{II} in the soln. $\times 10^4$. $[Sb_{II}] \times 10^4$.	G. mols. of lactate ion in the soln. $\times 10^4$. $[La^-] \times 10^4$.	K.
2.15	10.35	8.798	1.553	29.32	0.435
2.20	10.35	7 763	2 587	32.80	0.641
2.25	10 35	7.245	3.105	36.47	0.657
2.30	10.35	6·727	3.623	41.01	0.659
2.35	10.35	6.210	4.140	45.80	0.650
2.40	10.35	5.382	4.968	51.14	0.719
2.45	10.35	4 140	6.210	57.07	0 032
				Mean	0 67

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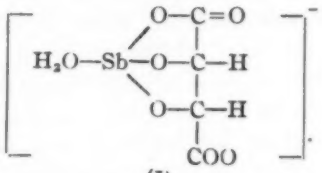
TARTRATE COMPLEX OF TRIVALENT ANTIMONY. PART I

By K. C. Samantora, D. V. Raman Rao and S. Pani

The variation of p_H on neutralisation of tartaric acid containing a small amount of antimony chloride under identical conditions has been studied. Two equivalents of acid per atom of antimony were observed to be liberated. Both the hydroxyl groups of tartaric acid are assumed to take part in the reaction for the formation of antimonyl tartrate ion.

Considerable amount of work has been done on tartar emetic. The complex ion has been suggested (Reihlen and Hezel, *Annalen*, 1931, **487**, 213) to be



(I)

Very little quantitative work has, however, been done. The following work was undertaken to deduce quantitatively if the alcoholic groups of tartaric acid took part in the reaction for the formation of the complex antimonyl tartrate ion.

Tartaric acid is a dibasic acid. If a complex of the above type is formed it would behave as a tetrabasic acid. If a suitable compound of antimony is added to tartaric acid or partially neutralised tartaric acid, so that no hydrolysis takes place and formation of the complex goes almost to completion, two equivalents of acid per atom of antimony would be liberated and the p_H of the system would be accordingly decreased. The reaction can be represented as:

$$SbCl_3 + \begin{matrix}COO^{2-}\\|\\(CH.OH)_2\\|\\COO\end{matrix} + H_2O \rightleftarrows (I)^- + 2H^+ + 3\,Cl^-$$

$$\text{or} \quad SbCl_3 + \begin{matrix}COO^{-}\\|\\(CH.OH)^2\\|\\COOH\end{matrix} H_2O \rightleftarrows (I)^- + 3H^+ + 3Cl^-$$

$$\text{or} \quad SbCl_3 + \begin{matrix}COOH\\|\\(CH.OH)_2\\|\\COOH\end{matrix} + H_2O \rightleftarrows (I)^- + 4H^+ + 3\,Cl^-$$

Whichever reaction takes place, the net excess of acid liberated is equal to two equivalents of acid per atom of antimony.

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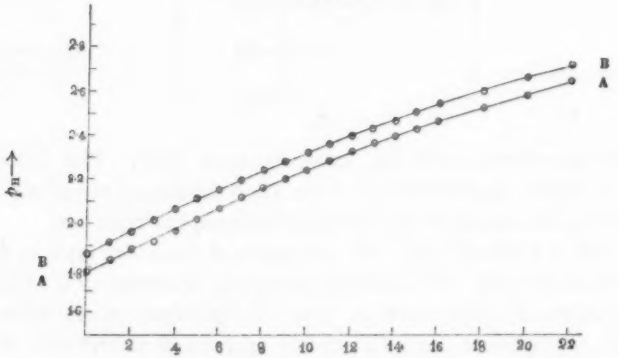
EXPERIMENTAL

Analar quality antimony chloride was dissolved in 3.471*N*-HCl. There was no hydrolysis. The antimony content of the solution was determined by titrating a known volume of the solution against standard bromate solution ; 25 ml. of this solution ($4.14 \times 10^{-2}M$) was mixed with 240 ml. of 0.185 *M* tartaric acid and 87.5 ml. of 0.9917 *N*-NaOH solution ; the NaOH was added to neutralise all the free HCl in the solution. The p_H of this solution was measured by the Marconi p_H meter. Increasing amounts of sodium hydroxide solution (0.9917 *N*) were added and the p_H was measured after stirring. The results are graphically represented by curve A in Fig. 1.

In another experiment 25 ml. of 3.471 *N*-HCl solution was mixed with 240 ml. of 0.185*M* tartaric acid and 87.5 ml. of 0.9917*N*-NaOH solution. The p_H was measured as before. The results are shown in curve B, Fig 1.

FIG. 1



Large amount of tartaric acid compared to the concentration of antimony chloride was used so that the formation of the complex would be complete and there would be no hydrolysis on neutralisation of free HCl. Besides, the amount of HCl liberated due to the formation of the complex would be very small compared to the free tartaric acid present in the solution ; hence there would be practically no change in the nature of neutralisation curve of tartaric acid. The amount of tartrate ion in the complex would be so small that it could be neglected compared to free tartaric acid. When a small amount of alkali is added to the complex, which is small compared to tartaric acid, formation of the complex is not effected and the alkali neutralises the free tartaric acid.

The horizontal distance between the two curves indicates the amount of alkali which is to be added to the system containing antimony chloride so that the p_H of the two systems would be the same. This is therefore equal to to the amount of acid liberated due to the formation of the complex. It is of interest to note that the horizontal distance between the two curves is constant. Two equivalents of acid per atom of antimony is liberated. It is therefore concluded that both the hydroxyl groups of tartaric acid take part in the reaction as stated before.

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ESTIMATION OF THORIUM BY ORGANIC REAGENTS. PART VI. USE OF SOME IODOBENZOIC ACIDS

By Sachindra Kumar Datta and Gurupada Banerjee

Three iodobenzoic acids, namely, *m*-iodo-, 2-hydroxy-3 :5-di-iodo- and 2 :3 :5-tri-iodobenzoic acids, have been used for the estimation of thorium at p_H values ranging from 2.8, 3.2, 3.0 and 3.5 to 6, respectively. These can separate thorium from the cerite earths and from monazite extract by double precipitation method and a large number of metallic ions do not interfere in the estimation.

Several substituted benzoic acids, including benzoic acid itself, have been utilised as precipitants for thorium by various workers. The use of benzoic acid as a precipitating agent for thorium was first mentioned by Kolb and Ahrle (*Z. angew. Chem.*, 1905, **18**, 92) and Neish (*Chem. News*, 1904, **90**, 196) but was discarded as unsuitable. Rao (this *Journal*, 1950, **27**, 83), however, found that thorium could be completely separated from a mixture of cerite earths, rendered faintly acidic to methyl red, by adding a hot 1% benzoic acid solution followed by 5% ammonium acetate. After dissolving this precipitate in dilute nitric acid thorium was completely recovered by following the same procedure. Ammonium benzoate was also used by the above author with success. Benzoic acid was later recommended by Ventkatramaniah, Rao and Rao (*Anal. Chem.*, 1952, **24**, 747 ; *J. Sci. Ind. Res.*, 1951, **10B**, 254) for the separation of thorium from uranium and rare-earth elements. This reagent has also found application in precipitating thorium and zirconium from slightly acid solutions of the magnesium alloy and subsequently isolating thorium by precipitating as oxalate (Wengert *et al.*, *Anal. Chem.*, 1952, **24**, 1636). The use of substituted benzoic acids, like *m*-hydroxy-(Desmukh and Xavier, this *Journal*, 1952, **29**, 911), *o*-chloro-, *o*- and *p*-amino-benzoic acids, *o*-toluic and *m*-nitrobenzoic acids etc. (Rao *et al.*, *ibid.*, 1950, **27**, 457, 569, 610) for the estimation of thorium has been also recorded.

It has now been found that some substituted iodobenzoic acids, namely, *m*-iodo-, 2 :3 :5-tri-iodo- and 2-hydroxy-3 :5-di-iodo-benzoic acids, show definite promise as precipitating agents for thorium ion. Ignition of the thorium benzoates to thoria yields analytical results which compare favourably with those obtained by other suitable reagents in use, for the estimation of thorium. These acids, when employed in the form of their sodium salts, require a little higher p_H for the precipitation of thorium. They can separate thorium by double precipitation from the cerite earths ; a few metallic ions, however, interfere in the separation of thorium when present in a mixture.

Experimental

m-Iodobenzoic acid was obtained by diazotising 5-iodoanthranilic acid, prepared according to the method of Wallingford and Kruegar (Organic Synthesis, Coll. Vol. II, p. 349), and refluxing the diazonium compound with 95% ethyl alcohol mixed

with a trace of finely ground copper sulphate, following the same procedure as described by the above authors (*ibid.*, p. 353). The crude product was purified by recrystallisation of its ammonium salt. To 25 g. of the acid in a beaker was added 20 c.c. of hot water and the acid was partially neutralised with 6 c.c. of conentrated ammonia unlil the acid was completely dissolved after continuous stirring at 80°. The solution was then decolorised by heating with charcoal and filtered over a Büchner. The filtrate on cooling gave ammonium *m*-iodobenzoate crystals which were then dried. The free acid was obtained by dissolving the pure ammouium salt in 4 times its weight of water, precipitating the acid with HCl (conc.), adding ice to reduce the temperature to 20°, filtering by suction, washing with water and drying at 90°-110°. The purity of the acid was established from its m.p., 187-88°.

2-*Hydroxy*-3 : 5-*di-iodobenzoic acid*.—A solution of salicylic acid (0.18*M*) in glacial acetic acid was stirred in a solution of 0.38*M* of ICl in glacial acetic acid. On adding water to this solution a yellow precipitate of di-iodosalicylic acid appeared, which was then heated to 80° for 20 minutes and after cooling to room temperature the precipitate was filtered over a Büchner, washed and recrystallised from acetone to the constant m.p. of 235-36°.

2:3:5-Tri-iodobenzoic acid of B.D.H. reagent grade was employed for the determination of thorium.

The sodium salts of these acids were prepared by dissolving definite amounts of these acids in the requisite amounts of dilute sodium carbonate solution with the aid of heat, till neutral. The solutions were filtered. Na- salt of 2-hydroxy-3 : 5-di-iodobenzoic acid separated on cooling in the form of crystals, which were filtered. A solution of this sodium salt was prepared in hot water for the estimation. The sodium salts of the other acids remained in solution on cooling, which were therefore used as such.

Stock solutions of thorium, cerium and lanthanum were prepared and their earth contents determined as before (Datta and Banerjee, this *Journal*, 1954, **31**, 149).

Estimation of Thorium

These iodo-acids being practically insoluble in water, their sodium salts were employed for analysis. Alcoholic (50%) solutions of *m*-iodo- and tri-iodobenzoic acids and ammonium salt of *m*-iodobenzoic acid were also used.

Procedure.—To aliquot quantities of thorium nitrate solutions, rendered neutral to Congo red, was added hot 1% solution of the sodium salt of these iodo-acids, separately, in 250 c.c. beakers, followed by 10 c.c. of a 5% solution of ammonium acetate. A flocculent precipitate appeared at once which became more granular on digestion for about 5 minutes. The colour of the precipitates with *m*-iodo, di-iodo-hydroxy- and tri-iodobenzoic acids is pale pink, very pale yellow and red respectively. The precipitates which settled within 2 minutes, when filtered through a No. 42 Whatman filter paper, were washed with 1% solution of ammonium chloride and then partially dried in air and finally ignited to thoria. Similar precipitates were also obtained when 2% alcoholic (1 : 1) solutions of tri-iodo acids and NH_4-salt (1%) of *m*-iodobenzoic

acids were employed. But the alcoholic solution of *m*-iodobenzoic acid produced a gelatinous precipitate, which did not turn granular even on digestion with ammonium chloride, and presented a problem in filtration. The gelatinous precipitate was allowed to settle and the supernatant liquid was poured through the filter paper. After the liquid had been removed as much as possible, the precipitate was agitated with filter pulp to facilitate further filtration. The precipitate was similarly washed, dried and ignited. Table I records some of the results of estimation, each datum represents the mean of three estimations. It appears from the table that complete precipitation of thorium does not take place when its concentration in solution is less than 0.0023 g. to 0.0027 g. of thoria.

TABLE I

Estimation of thorium with the iodobenzoic acids.

Reagents employed.	ThO_2.		Diff.	Nature of the precipitate.
	Taken.	Found.		
m Iodobenzoic acid (alcoholic soln.)	1. 0.0272 g.	0.0272 g.	±0.0 mg.	Pale pink, gelatinous
	2. 0.0027	0.0025	−0.2	
Do (Na salt)	1. 0.0272	0.0271	−0.1	
	2. 0.0027	0.0026	−0.1	Pinkish white, flocculent
Do (NH_4 salt)	1. 0.0272	0.0273	±0.1	
	2. 0.0027	0.0026	−0.1	Do
2-Hydroxy-3:5-di iodobenzoic acid (alcoholic soln.)	1. 0.0272	0.0273	+0.1	Very pale yellow and granular
	2. 0.0027	0.0025	−0.2	
Do (Na salt)	1. 0.0408	0.0408	±0.0	Yellowish white
	2. 0.0027	0.0026	−0.1	
Tri-iodobenzoic acid (alcoholic soln.)	1. 0.0136	0.0134	−0.2	Grey white
	2. 0.0027	0.0024	−0.3	
Do (Na salt)	1. 0.0272	0.0270	−0.2	Pure white
	2. 0.0027	0.0026	−0.2	

Influence of Hydrogen-ion Concentration in the Precipitation of Thorium.—To find out the suitable p_H ranges for the quantitative precipitation of thorium by these reagents, estimations were carried out in solutions having different p_H values. The addition of the proper amounts of ammonium acetate was found essential to buffer the mixture and for the coagulation of the precipitates. Only the sodium salts were employed for such studies. The results are shown in Table II.

TAALE II

Effect of p_H on the precipitation of thorium.

ThO_2 taken = 0.0544 g. Total volume of the soln. = 75 c c.

ThO_2 obtained (in g.) by :	the thorium solution of p_H							
	1.6.	1 8.	2.0	2.4.	2.8.	3.0.	3.2.	3.5
Na *m*-iodobenzoate	0.0497	0.0508	0.0532	0.0538	0.0544	0.0543	0.0543	0.0545
Na hydroxy-di-iodobenzoate	0.0501	0.0510	0.0519	0.0522	0.0530	0.0539	0.0543	0.0544
Na tri-iodobenzoate	0.0504	0.0512	0.0513	0.0521	0.0532	0.0543	0.0543	0.0545

Separation of Thorium from a Mixture of Cerite Earths.—The sodium salts of these acids were employed for the separation of thorium from artificial mixtures containing thorium-cerium and thorium-cerium-lanthanum in varying amounts. From the preliminary studies it was seen that thorium could be separated by these reagents in the same p_H ranges as were found suitable for the estimation of thorium when present alone (vide Table II), only on adopting the double precipitation method; single precipitation showed slight contaminations. Some of the representative results are recorded in Table III.

TABLE III

No.	ThO_2 taken.	CeO_2 added.	La_2O_3 added.	ThO_2 obtained by Single pptn.	Double pptn.
		(a) Sodium salt of *m*-iodobenzoic acid.			
1.	0.0544 g.	0.0172 g.	...	0.0568 g.	...
2.	,,	...	0.0120	0.0559	...
3.	0.0272	0.0688	0.0480	...	0.0273 g.
4.	,,	0.1032	0.0720	...	0.0275
5.	0.0136	0.1032	0.0360	...	0.0138
6.	,,	0.1548	0.0120	...	0.0447
		(b) Sodium salt of 2-hydroxy-3 : 5-di-iodobenzoic acid.			
1.	0.0544	0.0172	—	0.0545	...
2.	0.0544	...	0.0120	0.0546	...
3.	0.0272	0.0688	0.0480	...	0.0272
4.	0.0136	0.1032	0.0360	...	0.0157
5.	,,	0.1548	0.0120	...	0.0139
6.	,,	,,	0.0360	...	0.0142
		(c) Sodium salt of 2:3:5-tri-iodobenzoic acid.			
1.	0.0544	0.0172	...	0.0548	...
2.	,,	...	0.0120	0.0546	...
3.	0.0272	0.1032	0.0720	...	0.0273
4.	0.0136	0.1032	0.0360	...	0.0137
5.	,,	0.1548	0.0120	...	0.0139
6.	,,	,,	0.0360	...	0.0149

Composition of the Thorium Precipitates.—The thorium salts of *m*-iodo- and tri-iodobenzoic acids were separately washed with hot water and then several times with hot alcohol in a No. 3 glass sintered crucible. The thorium precipitate with 2-hydroxy-di-iodobenzoic acid was first washed with hot water and then with hot acetone to remove the free acid. These were then dried in an electric oven at 105°-110° to a constant weight. Weighed amounts of the dried salts were then ignited to the oxide. The amounts of iodine present in these dried salts were also estimated by Piria and Schiff's method. The results of analysis with different samples, as recorded in Table IV, give an idea of the composition of the thorium salts of these acids.

TABLE IV

Th-salt dried at 105°-110°.	ThO_2 Found on ignition.	ThO_2 Calc from the wt. of the salt.	Amount of I_2 in the dried salt Found.	Amount of I_2 in the dried salt Calc.	Probable composition.
		Th-iodobenzoate.			
0.0783 g.	0.0271 g.	0.0272 g.	0.0262 g.	0.0261 g.	
0.0784	0.0274	0.0272	0.0260	0.0261	$(C_7H_4O_2I)_2$·Th(OH)$_2$
		Th *m* hydroxy-di-iodobenzoate.			
0.1458	0.0271	0.0272	0.0782	0.0784	$(C_7H_3O_3I_2)_3$·Th(OH)
0.1455	0.0270	0.0271	0.0783	0.0783	
		Th-tri-iodobenzoate.			
0.1302	0.0270	0.0272	0.0785	0.0784	
0.1303	0.0272	0.0272	0.0783	0.0784	$(C_7H_2O_2I_3)_2$·Th(OH)$_2$

Interferences in presence of other Elements

These iodobenzoic acids can separate thorium from a large number of elements within their respective p_H ranges. Some, however, require a double precipitation. The results have been indicated in Table V. The elements interfering in the separation have also been mentioned therein.

TABLE V

ThO_2 taken = 0.0816 g.

Oxide added.	ThO_2 obtained by sodium salt of *m*-Iodobenzoic acid.	2-Hydroxy-di-iodobenzoic acid.	Tri-iodobenzoic acid
BaO, 0.2310 g.	0.0823 g.	0.0819 g.	0.0817 g.
CaO, 0.1942	0.0814	0.0817	0.0816
SrO, 0.2047	0.0814	0.0817	0.0815
MgO, 0.1635	0.0821	0.0819	0.0817
ZnO, 0.2417	0.0820	0.0821	0.0814
*NiO, 0.2341	0.0823	0.0822	0.0819
*CoO, 0.2136	0.0826	0.0821	0.0821
*Cr_2O_3, 0.1904	0.0820	0.0822	0.0818
Al_2O_3, 0.2213	0.0821	0.0819	0.0818
* MnO, 0.2130	0.0824	0.0818	0.0819
Metals tested for interference:			
Fe^{2+} ...	−	+	+
Fe^{3+} ...	+	+	+
Zr^{4+} ...	+	+	+
Ti^{3+} ...	−	+	−
Hg^{2+} ...	+	+	+
Hg_2^{2+} ...	+	+	+
UO_2^{2-} ...	−	+	−

* Indicates double precipitation.
\+ „ interference.
− „ non-interference.

Estimation of Thorium in Monazite Sand

The acid extract of monazite, prepared and freed from zirconium etc. in the usual manner (Raghava Rao *et al.*, this *Journal*, 1950, **27**, 458), was neutralised to proper p_H values suitable for the reagents, and thorium was estimated. The results after comparing with those obtained by *m*-nitrobenzoic acid are shown in Table VI.

TABLE VI

No.	Wt. of the sample.	*m*-Nitrobenzoic acid.		*m*-Iodobenzoic acid.	
		ThO_2 obtained.	$\%ThO_2$.	ThO_2 obtained.	$\%ThO_2$.
1.	1.232 g.	0.0902 g.	7.32	0.0901 g.	7.31
2.	1.255	0.0918	7.32	0.0916	7.31
3.	1.320	0.0965	7.31	0 0964	7.30
		2-Hydroxy-di-iodobenzoic acid.		Tri-iodobenzoic acid.	
1.	1.232	0 0900	7.30	0.0901	7.31
2	1.255	0.0916	7.31	0.0917	7.31
3.	1.320	0.0964	7.30	0.0965	7 31

DISCUSSION

Among the different iodobenzoic acids studied, their sodium salts have been found to be most suitable for the quantitative determination of thorium. Addition of suitable electrolytes, like ammonium acetate, ammonium chloride, etc. is essential for the precipitation of thorium by these reagents, excepting the case of sodium salt of *m*-iodobenzoic acid, which forms the granular thorium salt even in the absence of any electrolyte. Thorium salts of all the three acids being basic type of compounds, thorium cannot be estimated by direct weighing, and hence, ignition of the precipitates to thoria is necessary. From the p_H studies, it has been observed that thorium can be determined from its solutions with the sodium salt of *m*-iodobenzoic acid in a more wider p_H range starting from 2.8 onwards, whereas the sodium salts of 2-hydroxy-di-iodo- and tri-iodobenzoic acids begin to precipitate thorium quantitatively from p_H 3.2 and 3.0 respectively. These reagents can also separate thorium suitably from the cerite earths on adopting double precipitation method. The sodium salts of 2-hydroxydi-iodobenzoic acid and tri-iodobenzoic acid are better in this respect than the corresponding salt of the *m*-iodo-acid, the former two can separate thorium by double precipitation from a mixture having thoria-rare earth oxide ratio 1 : 12, whereas the corresponding ratio with the latter is 1 : 10. For the effective separation of thorium from monazite sand by these reagents double precipitation is necessary. They can also separate thorium from a number of metallic ions normally appearing with thorium, the presence of some requiring double precipitation. Zirconium and iron could not be separated from thorium even on p_H adjustment.

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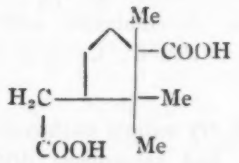
A NEW SYNTHESIS OF *di*-CAMPHONONIC ACID*

By J. K. Roy

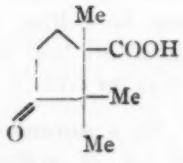
dl-Camphononic acid has been synthesised by methylation of 1:2-dimethyl-1-carbethoxy*cyclo*pentan-3-one after protecting the reactive methylene group with a methylanilinomethylene residue, followed by the removal through a basic hydrolysis.

For an unambiguous synthesis of homocamphoric acid (I), Ganguly (this *Journal*, 1943, **20**, 101) first synthesised camphononic acid (II) (cf. Lapworth and Chapman, *J. Chem. Soc.*, 1899, **75**, 985; Lapworth, *ibid.*, 1900, **77** 1070), an important degradation product of camphor. Further, it was shown by Ganguly (*loc. cit.*) that the synthesis of homocamphoric acid might be achieved from this by introducing an acetic acid residue at the site of the carbonyl group.

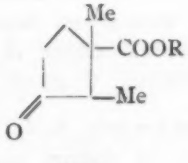
In the present investigation a convenient synthesis of camphononic acid (II) has been achieved by methylation of 1:2-dimethyl-1-carbethoxy*cyclo*pentan-3-one (III, R=Et) after protecting the methylene group with a methylanilinomethylene residue that could be easily removed (Birch and Robinson, *J. Chem. Soc.*, 1944, 501; Birch, Jaeger and Robinson, *ibid.*, 1945, 582).



(I)



(II)



(III)

The starting material (III) was prepared previously by Chakravarti (this *Journal*, 1913, **20**, 247). It has now been prepared with some modifications in the experimental procedure. Ethyl $\alpha\beta$-dicyano-β methylbutane-$\alpha\delta$-dicarboxylate (Banerjee, *ibid.*, 1940, **17**, 426) has been methylated following the method of Miller, Scholl and Long (*J. Amer. Chem. Soc.*, 1951, **73**, 5608) using dimethyl sulphate and alkali instead of sodium ethoxide and methyl iodide (Chakravarti, *loc. cit.*). The corresponding triethyl ester on the Dieckmann condensation and hydrolysis yields the *cyclo*pentanone carboxylic acid derivative (III, R=H) in 80% yield.

The corresponding ester (III, R=Et) is then formylated with ethyl formate in presence of alcohol-free sodium methoxide and the crude formyl derivative condensed with methylaniline; the resulting methylanilinomethylene compound without further purification is methylated with potassium *tert.*-butoxide in *tert.*-butyl alcohol and methyl iodide (Johnson and Posvic, *J. Amer. Chem. Soc.*, 1947, **69**, 1361). The

*An advanced communication was published in *Science & Culture*, 1953, **19**, 49; another communication along similar lines but differing in experimental details was also published by Bagchi and Talukdar, *ibid.*, 1953, **18**, 500.

blocking group is then removed in a single step by refluxing with a 20% KOH solution (Woodward *et al.*, *ibid.*, 1952, **74**, 4223), and camphononic acid (II) isolated after acidification of the alkaline hydrolysis product in an overall yield of 17-20%.

EXPERIMENTAL

γ-Methylpentane-αγδ-tricarboxylic Acid.—Ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate (Banerjee, *loc. cit.*) (55.8 g.) was dissolved in alkali (8.4 g. of sodium hydroxide in 45 c.c. of water) and to the mechanically stirred solution dimethyl sulphate (26.46 g.) was added during 45 minutes. The rate of addition was such that the temperature of the mixture remained at 45°-47°, basic condition being maintained throughout by the addition of alkali. When the addition was completed, the stirring was continued for 1½ hours more and the temperature was allowed to come down to 30°. It was then cooled with ice, and diute HCl added until the mixture was acidic to Congo red. The oily product after separation from the aqueous layer weighed 52.5 g. It was then hydrolysed by refluxing with eight times its volume of HCl (conc.) for 22 hours. It was ev porated to dryness and the crude gummy acid after drying was esterified by refluxing with ethanol (300 c.c.) and sulphuric acid (50 c.c., *d.* 1.8) for 36 hours. The ester after isolation in the usual way was distilled in vacuo as an oil, b.p. 146° – 148°/2 mm., yield 37 g. (58%). A portion of the above ester (4 g.) on hydrolysis with HCl (conc., 30 ml.) furnished γ-methylpentane-αγδ-tricarboxylic acid, which after three crystallisations from HCl (conc.) melted at 175°, yield 2.1 g. (75%). It showed no depression in melting point on admixture with a sample prepared by the method of Chakravarti (*loc. cit.*). (Found: C, 49.32; H, 6.39. Calc. for $C_9H_{14}O_6$: C, 49.54; H, 6.42 per cent).

dl-*Camphononic Acid* (II).—To a suspension of dry sodium methoxide (prepared from 2.3 g. of sodium and 32 c.c. of methanol, and subsequent drying under diminished pressure) in dry benzene (25 c.c.) freshly distilled ethyl formate (7.4 g.) was slowly added with stirring and the stirring continued for half an hour more. It was then cooled in an ice-bath and to it a solution of ethyl 2:3-dimethylcyclopentan-1-one-3-carboxylate (III, R = Et) (8.5 g.), prepared from ethyl γ-methylpentan-αγδ-tricarboxylate, following the method of Chakravarti (*loc. cit.*), in dry benzene (25 c.c.) was added with stirring. After completing the addition the ice-bath was removed and stirring continued for further 8 hours. Cold water was added to the reaction mixture and the aqueous layer was separated from benzene, and the benzene layer finally washed with a 2% KOH solution. The combined aqueous layer was cooled with ice and acidified with cold and dilute hydrochloric acid. It was then extracted with benzene-ether mixture. After evaporation of the solvent, the crude hydroxymethylene compound weighed 6.4 g. From the benzene layer 1.2 g. of the unchanged keto-ester was recovered.

The crude hydroxymethylene compound (6 g.) was dissolved in dry benzene (25 c.c.) and to it freshly distilled methylaniline (7 g.) was added at room temperature. The solution turned turbid. It was left as such for 16 hours; water separated out together with small amounts of yellow crystals which were brought to solution by

the addition of more benzene (25 c.c.), and the benzene evaporated over a period of 30 minutes. The excess methylaniline was removed by distillation under diminished pressure and the crude methylanilinomethylene derivative was used as such for the next step.

To the solution of potassium *tert.*-butoxide (prepared from 1.8 g. of potassium in 50 c.c. of dry *tert.*-butanol) the above methylanilinomethylene derivative, dissolved in *tert.*-butanol (30 c.c.), was added with stirring and the stirring continued for further 45 minutes. To the cooled solution methyl iodide (16 g.) was added dropwise and it was stirred at room temperature for 20 hours. Excess *tert.*-butanol was then removed under dimmished pressure from a steam-bath and the reaction mixture was diluted with water containing a little HCl followed by extraction with ether in the usual way. The ether extract was washed with water, and dried with anhydrous sodium sulphate. After removal of the ether, the blocking group was removed by refluxing the residue for 6 hours with a 20% KOH solution (6 g. KOH in 30 c.c. water). The cooled aqueous mixture was extracted with ether and the alkaline layer on acidification with HCl (dil.) was extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulphate. The ether was removed and the residue was distilled in vacuo furnishing camphononic acid, b.p. 143°-45°/2mm., which solidifed on cooling, yield 1g. (17-20% overall yield). It was crystallised four times from water containing a little ethanol, m.p. 229-30°. Ganguly (*loc. cit.*) records m.p. 230-31°. (Found : C, 63.2 ; H, 8.3. Calc. for $C_9H_{14}O_3$: C, 63.5; H, 8.2 per cent).

On refluxing an alcoholic solution of the acid with hydroxylamine hydrochloride and pyridine it formed an oxime. It melts after crystallisation from alcohol-water mixture at 187°. Ganguly (*loc. cit.*) records its m.p. as 189°.

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MIXTURES OF ARSENIC AND HYDROCHLORIC ACIDS IN GLACIAL ACETIC ACID

By Hussein Sadek

The conductance of arsenic acid solutions in glacial acetic acid was measured at 35°. Proton transfer between solvated hydrogen ions and neutral arsenic acid molecules is suggested to account for the high values of the equivalent conductances. Mixtures of hydrochloric and arsenic acids in glacial acetic acid showed conductances which were many times greater than the additive values. Transport number experiments showed that arsenic acid formed a positive ion in these mixtures.

In a previous communication the author showed that phosphoric acid formed a positive ion in glacial acetic acid solutions of hydrochloric acid (this *Journal*, 1952, **29**, 846). This investigation has been extended to acid mixtures containing arsenic and hydrochloric acids in glacial acetic acid.

Experimental

The preparation of pure glacial acetic acid and of solutions of hydrochloric acid was described previously (*loc. cit.*).

Crystals of arsenic acid, $As_2O_5.4H_2O$, were prepared according to a procedure laid down by Archibald ("Preparations of Pure Inorganic Substances", 1932). These were dissolved in glacial acetic acid to which quantities of acetic anhydride sufficient to react with the water of crystallisation were added and the solution was refluxed for 2 hours. Concentrated solutions prepared in this manner were unstable and precipitated after few days a gelatinous material. In this work freshly prepared dilute solutions were only used and were analysed by precipitation and ignition as magnesium pyroarsenate.

Mixtures of hydrochloric and arsenic acids in glacial acetic acid were prepared by admixing the two acid solutions directly into the conductivity cell and the mixtures were analysed for their acid constituents.

Conductance and transport number experiments were made at 35°, as described previously (Sadek, *loc. cit.*).

Discussion

Assuming as in the case of phosphoric acid solutions that arsenic acid behaves as a monobasic acid in glacial acetic acid, the equivalent conductance of the solutions is shown in Table I.

Table I

Equivalent conductance of arsenic acid.

$c \times 10^2$	...	2.984	3.221	6.914	8.584	12.53	14.24
Λ	...	0.36	0.46	1.02	1.27	1.68	1.94
$\Lambda\sqrt{c}$	...	0.0623	0.0800	0.2683	0.3715	0.5880	0.7362

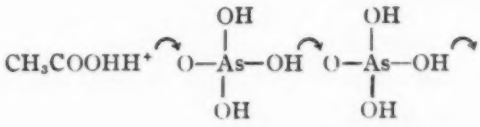
It can be seen that the conductance values increase regularly as the concentration of arsenic acid rises. A comparison of these values with those of phosphoric acid solutions at the same concentration shows that the conductance values of arsenic acid solutions are about two hundred times those of phosphoric acid solutions. These high conductance could be attributed in the first place to triple-ion formation in Fuoss' sense (Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387). However, this explanation is found untenable since triple-ion formation requires a straight line plot of $\Lambda\sqrt{c}$ against c according to the relation :

$$\Lambda\sqrt{c} = A + Bc,$$

where A and B are constants and have positive signs. The condition for the conductance minimum which corresponds to the formation of ion-pairs is given by $C_{min} = A/B$.

When $\Lambda\sqrt{c}$ is plotted against c, a straight line with a negative intercept is obtained. This behaviour indicates that triple-ions are not truly formed in solutions of arsenic acid in glacial acetic acid. The high value of the conductances is therefore due to a mechanism other than the formation of triple-ions.

Although phosphoric and arsenic acids possess the same electronic configuration, yet, Raman spectra reveal marked differences in the structures of the two acids. Phosphoric acid exists in the aci-form, $H_3(PO_4)$, in which the hydrogen atoms are more or less ionogenic and are not fixed with respect to certain oxygen atoms (Simon and Schulze, *Z. anorg. Chem.*, 1939, **242**, 313). In the case of arsenic acid, on the other hand, the three hydrogen atoms are attached to three oxygen atoms forming definite -OH groups (Feher and Morgenstern, *ibid.*, 1937, **232**, 169). The high conductance values of arsenic acid solutions can therefore be attributed to proton transfer between the solvated hydrogen ion and neutral arsenic acid molecules according the scheme :



Under these conditions the conductance of the solutions should increase regularly with increase of concentration.

The specific conductance of the mixtures of hydrochloric and arsenic acids in glacial acetic acid, which are shown in Table II, are compared with the additive values of the specific conductances of the single acids at the same molal concentration as that present in the mixture. In making these mixtures the concentration of arsenic acid was kept about 0.02 molal, while that of hydrochloric acid was varied from 0.04 to 0.14 *m*.

It can be seen from Table II that the observed specific conductances of the mixtures are many times greater than the calculated additive values. These large conductances are due to the interaction between the two acids to form conducting ions

in which arsenic acid is forming a positive ion in a similar manner to the mixtures of hydrochloric acid and phosphoric acid. Transport number experiments recorded in Table III confirm this view.

TABLE II

Sp. conductance of mixtures of hydrochloric and arsenic acids in glacial acetic acid.

a. m-HCl.	b. m-H_3AsO_4.	c. 10^4. k acl.	d. 10^4. $k_{H_3AsO_4}$	e. (c+d).	f. 10^4. $k_{obs.}$	g. (f/e.)
0.0477	0.0220	0 015	0.061	0.076	1.21	19.8
0.101	0 0225	0 025	0.063	0.088	4.09	46 6
0.1172	0.0344	0·027	0.140	0.167	6.84	41.0
0.1377	0.0264	0.029	0.083	0.112	5·96	53.2
0.1429	0.0196	0.030	0.005	0.135	2.33	67 0

TABLE III

Original soln.	Expt. 1.	Expt. 2.	Anode soln.	Expt. 1.	Expt. 2.
Wt of soln.	8.1760 g.	7.7504 g.	Wt. of soln.	25.2858 g.	21.4560 g.
Wt. of HCl	0.c281	0 01227	Wt. of HCl	0 0833	0.0406
Wt. of H_3AsO_4	0.0257	0.02195	Wt. of H_3AsO_4	0.0173	0.0137
Wt. of acetic acid	8.1227	7.7162	Wt. of acetic acid	25.1852	21.4017
			Loss in H_3AsO_4	0.0624	0.0472
			Ag deposited	0.2190	0.3290

The calculation of the transport number of the conducting ions was not possible since the equilibrium conditions for the formation of triple-ions in mixed acid solutions were uncertain.

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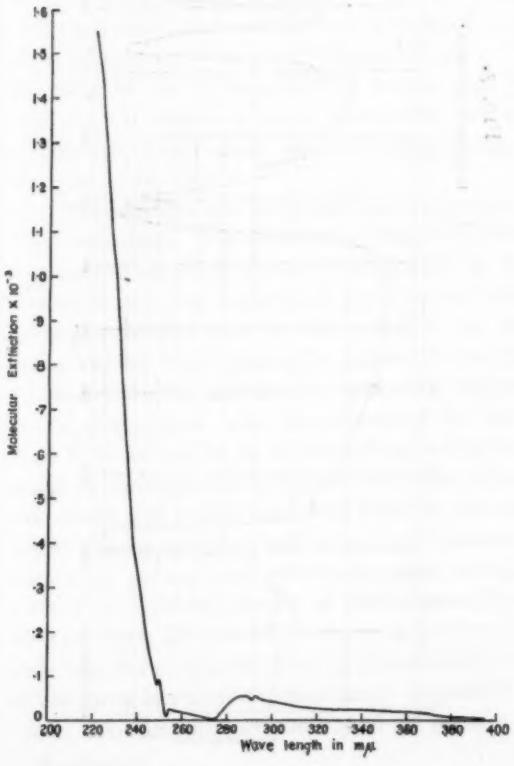
ON THE CONSTITUTION OF SWIETENINE: THE NON-BITTER PRINCIPLE OF THE SEEDS OF *SWIETENIA MACROPHYLLA*, KING

By Tarakeswar Chakravarty and Asima Chatterjee (Neè Mookerjee)

The properties of swietenine ($C_{18}H_{24}O_5$, m.p. 260, dec.), the non-bitter principle of *Swietenia macrophylla*, have been studied, and all its functional groups and its partial structure have been determined. From the spectroscopic observations coupled with chemical evidence it has been possible to assess the presence of a six-membered αβ-unsaturated lactone and a tertiary hydroxyl group in swietenine molecule. The substance has also been found to contain a ketonic and a methoxyl group. Kuhn-Roth experiment has further revealed the presence of two :CMe groups in the compound

Swietenia macrophylla King, closely related to *Swietenia mahogany* Jacq., belongs to *Meliaceae* family, which from a chemical standpoint has hardly been investigated. Earlier it was observed by one of the authors that *Swietenia macrophylla* contained in its seeds a bitter principle, swietenolide and swietenine, a non-bitter ingredient (Chakravarty and Guha Sircar, this *Journal*, 1951, **28**, 207). The properties and constitution of swietenine form the subject of the present communication.

Fig. 1



Swietenine and swietenolide have been isolated from *S. macrophyila* following the method described earlier. Homogeneous swietenine (m.p. 260°, dec.) has been prepared from the crude mixture of swietenine and swietenolide first by several fractional crystallisations from acetic acid and subsequently by the method of chromatographic adsorption over Merck's alumina using chloroform as the eluent. The empirical formula of swietenine, {$[\alpha]_D^{30} = +133.5°$ in 4.25% chloroform solution} that was earlier proposed as $C_{18}H_{24}O_5$ containing a methoxyl group has been confirmed from its conductometric titrations and molecular weight determination by Rast's method. Swietenine has been

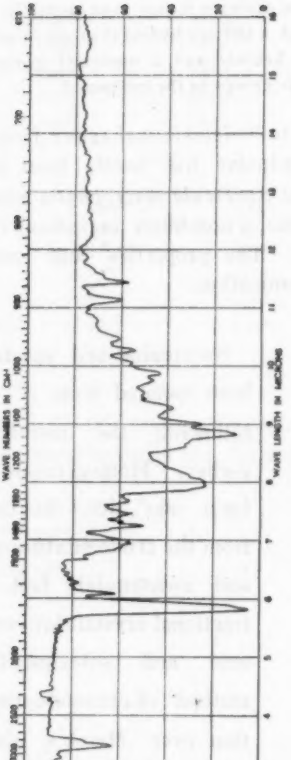


FIG. 2.
Sweetenine in Nujol mull.

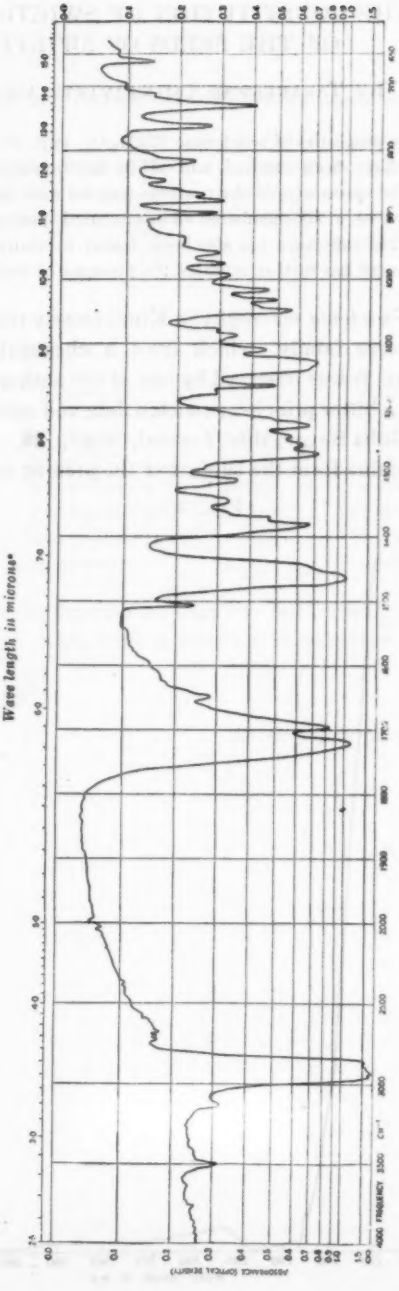


FIG. 3.
Wave length in microns.

subjected to spectral analyses - both ultraviolet and infra-red, which have afforded definitive information about the functional groups in the molecule as also its partial structure. The ultraviolet specturm of the compound has been examined in a Beckman quartz spectrophotometer (Model Du) in ethanol (Fig. 1). It shows absorption maxima at 288 mμ characteristic of an isolated carbonyl group (-C=O-) (Clemo and Cocker *J. Chem. Soc.*, 1946, 33) , the maxima for conjugated carbonyl (-C=C-C=O) generally appearing in the U. V. spectrum at 236-241 mμ (Karrer *et al.*, *Helv. Chim. Acta* 1954, **37**, 790). The U. V. curve also exhibits an intense absorption at the region 218-220 mμ with no maxima. This is precisely the region where αβ-unsaturated lactones exhibit high intensity of absorption with maxima or no maxima (Haynes and Jones, *J. Chem. Soc.*, 1952, 4721; Dauben and Hance, *J. Amer. Chem. Soc.*, 1953, **75**, 3352; Ruzicka, Plattner and Heusser, *Helv. Chim. Acta*, 1942, **25**, 435; Clemo and Cocker *loc. cit.*), the former being discernible in a very few cases. These observations lead to the conclusion that two of the oxygen atoms in swietenine form part of an αβ-unsaturated lactone ring as one of its chromophoric groups. Chemical evidence of this lactone group has been obtained from saponification experiments. With a view to obtaining further insight into the molecular structure of the compound, its infra-red absorption spectrum has been carefully studied in Nujol mull with a Baird Infra-red double beam spectrophotometer (Fig.). From the spectrum it would be evident that there is a sharp and well-defined absorption band at 1724 cm^{-1} (compared with the value of 1725 cm^{-1} for an αβ-hexenolactone). This affords a positive evidence of the presence of an αβ-unsaturated-δ-lactone ring in swietenine and not βγ-lactone which exhibits an intense infra-red absorption at 1782cm^{-1} (Barton, Jeger, Prelog and Woodward, *Exper.*, 1947, **3**, 83; Djerassi, Sengupta, Herran and Walls, *J. Amer. Chem. Soc.*, 1954, **76**, 2966).

The infra-red and ultraviolet spectral properties of swietenine are thus found to be fully consistent. The observation that swietenine possesses an αβ-unsaturated hexenolactone and not βγ, is further strengthened by its inertness towards aniline, alcoholic hydrochloric acid and ammoniacal silver nitrate solution. Swietenine contains an ethylenic bond as evidenced from the appearance of an intense I R. band at 6.1 μ. The band for a double bond generally appears in the I.R. spectrum at 6.04 μ. In swietenine it has been found to shift at 6.1 μ indicating that it is conjugated. This double bond must be in conjugation with the carbonyl of the lactone group (-O-CO-) (as previously stated from U.V. curve) *i.e.* in its αβ-position and not in conjugation with the other carbonyl group in the compound which is found to be isolated (*vide supra*). All attempts to reduce this conjugated double bond with Pd/C or with Adam's PtO_2 catalyst in acetic acid medium at room temperature and atmospheric pressure have failed. Similar difficulties are frequently encountered with compounds having double bonds in the αβ-position with respect to carbonyl groups of the lactones (Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15**, 431; 1937, **20**, 1271). However, a positive evidence of −C=C− group in swietenine has been secured from its yellow coloration with tetranitromethane in chloroform as also from bromination experiment. It readily forms a dibromide ($C_{18}H_{24}O_5Br_2$, m.p. 170°). The presence of double bond is further corroborated by Winkler's experiment

(Stoll, Hofmann and Kreis, *ibid.*, 1934, **17**, 1344). The infra-red spectrum of swietenine dibromide is found to lack the peak absorption at 6.1 μ, indicating that the olefinic double bond has disappeared. This is exactly what is expected if the double bond in swietenine undergoes bromine addition.

Of further interest is the position of the rather strong and sharp (not broad) infra-red bands at 2.95μ and 8.6 μ respectively, to be ascribed to a tertiary hydroxyl group (Sexton and Britton, *J. Amer. Chem. Soc.*, 1948, **70**, 3607). These spectral evidences together with Zerewitinoff's determination of one active hydrogen atom in the compound confirm the presence of a hydroxyl group in swietenine. But it did not produce any crystalline acetyl derivative under various acylating conditions tried. The gummy reaction product left after acylation was examined in a Baird infra-red double beam spectrophotometer. The spectrum did not show any peak absorption for hydroxyl group but exhibited a characteristic band for acetyl group at 8.1 μ indicating that the hydroxyl group in swietenine did undergo acylation. Attempts to prepare the gummy acetyl derivative in a crystalline state by the method of chromatographic adsorption over alumina and celite respectively met with failure. Swietenine repels dehydration. Thus from the resistance to dehydration, as also oxidation, it seems that the hydroxyl group is most plausibly tertiary. This suggestion is made following its analogy with aconite alkaloids (Jacobs and Pelletier, *J. Amer. Chem. Soc.*, 1954, **76**, 161).

The failure to obtain red coloration with swietenine by methyl alcoholic caustic potash solution (5%) probably points to the absence of hydroxyl group in the γ-carbon atom (allyl position with respect to the double bond in the lactone ring ; *Helv. Chim. Acta*, 1951, **73**, 677). If the hydroxyl group be assumed to be located in the α, β or δ carbon atom in the lactone ring, it is expected to yield a keto or an enolised keto-acid on alkali hydrolysis. Since swietenic acid obtained from swietenine upon saponification possesses neither any ketonic character nor gives any coloration with alcoholic ferric chloride solution for enolic groups, it is reasonable to believe that the hydroxyl group present in the molecule is attached to the main nuclear structure but not in the lactone ring like andrographolide (Karrer, Biswas and Schwyzer, *ibid.*, 1951, **73**, 662).

Swietenine does neither reduce Fehling's solution and ammoniacal silver nitrate solution nor does it respond to the Angeli-Rimini test. The infra-red spectrum of the compound also lacks the peak absorption for an aldehyde at 3.86 μ. Therefore, these are sufficient reasons to eliminate the possibility of the aldehydic function of the fifth oxygen atom out of primary consideration. But swietenine does contain a carbonyl group (cf. U.V. spectrum, *vide supra*) other than the carbonyl of the lactone. This must be therefore a ketone. Chemical evidence of this ketone group in swietenine has been presented by the formation of 2 : 4-dinitrophenylhydrazone, $C_{18}H_{34}O_4N{=}NH{-}C_6H_3(NO_2)_2$, m.p. 182° although the substance fails to produce any oxime or semicarbazone. It readily forms pyrylium salts, thereby showing that the ketone is associated (Desai and Wali, *Proc. Ind. Acad. Sci.*, 1937, **6A**, 135). This methylene group with an active CH_2- group, however, fails to produce any condensation product with benzaldehyde or acetone.

A Kuhn-Roth experiment has been carried out with the compound which reveals the presence of two ⋮C-Me groups, the qualitative detection of which has been possible from the presence of its characteristic absorption peak at 7.21 μ (Fig. 2).

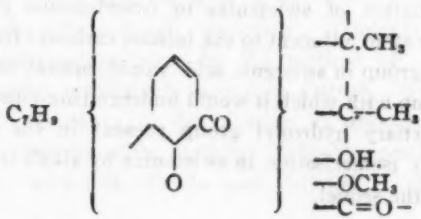
To secure further information on the constitution of swietenine, its degradation experiments have been carried out under mild conditions. Action of alkali on swietenine has been studied. It is found to have dual functions, namely lactone-opening and isomerisation. Alcoholic alkali readily opens the lactone ring at moderately elevated temperature (vide experimental) and the hydroxy-acid, swietenic acid ($C_{18}H_{26}O_6$, m.p. 208-10°, dec.) so formed on heating with dilute hydrochloric acid undergoes ring-closure furnishing a neutral compound ($C_{18}H_{24}O_5$, m.p. 262°, dec.) which is isomeric with swietenine. Their U.V. spectra are practically identical, having the same absorption maxima and minima. This compound has been designated as *iso*swietenine. Now, the base-catalysed transformation of swietenine to *iso*swietenine could be due either to inversion of the carbon atom adjucent to the lactone carbonyl function, *i.e. cis trans* isomerisation, when $-CO_2H$ group in swietenic acid would appear in the same plane as that of the tertiary -OH group with which it would undergo ring-closure or due to simple relactonisation with the tertiary hydroxyl group present in the original compound. The possibility of *cis-trans* isomerisation in swietenine by alkali treatment is ruled out as it would be evident from the sequel.

The fact the *cis*-orientation of the C atoms at the double bond in swietenine has not been disturbed is indicated by the absence of a band at 965 cm^{-1} in it (characteristic of *trans*-orientation) in *iso*swietenine (Fig. 3) and also by the presence of a band therein at 700 cm^{-1} (characteristic of *cis*-orientation) which is discernible in the original compound, swietenine (Fig. 2) (Tipson and Clapp, *J. Org. Chem.*, 1953, **18**, 958). Ultraviolet spectra of *iso*swietenine and swietenine are exactly the same. Their infra-red spectra are very similar, pointing out that swietenine has not undergone any fundamental changes in structure during saponification. *iso*Swietenine does contain a methoxyl and an isolated ketone, a hydroxyl group and two ⋮C.Me groups as also an $\alpha\beta$-hexenolactone. From all these evidences it can be assessed that there has been no *cis-trans* isomerisation and no vital change in molecular structure in swietenine during its alkali treatment and its conversion into *iso*swietenine. It is simply a relactonisation with the tertiary hydroxyl group. Thus participation of this hydroxyl group is responsible for the isomeric change during ring-closure of swietenic acid to the *iso*-compound. Relactonisation of swietenic acid to *iso*swietenine and their infra-red spectra adduce further information that the lactonic hydroxyl and carbonyl groups and the free tertiary hydroxyl group present in the original compound, swietenine, are all co-planar.

Experiments with diazomethane have been tried with a view to investigating whether swietenine does form a pyrazoline derivative. This study seems to be quite pertinent in this system as $\alpha\beta$-unsaturated lactone readly forms pyrazoline derivative with diazomethane. This reagent reacts with swietenine but forms an intractable gum which could not be made crystalline using various techniques.

Swietenine contains a methoxyl group. But the percentage of methoxyl is found to be always lower than the theoretical value from which it will be quite reasonable to assume that the position of the methoxyl group is appreciably hindered. Demethylation of certain veratrole derivatives and related ethers can be effected with warm acids under comparatively mild conditions (Robertson *et al.*, *J. Chem. Soc.*, 1915, **107**, 257; 1950, 3435). In our case elimination of methoxyl group with warm acids failed, indicating the absence of methoxy benzenoid system in swietenine. With hydriodic acid (*d* 1.7) and with anhydrous aluminium chloride demethylation has been found to occur in swietenine, but only partially, when heated for 12-18 hours.

From all the available evidences spectral and chemical, a partial structure of swietenine may be postulated as:



Further exploratory experiments to find out its complete structure are in progress.

EXPERIMENTAL

Isolation of Homogeneous Swietenine.—Swietenine and swientenolide were isolated from *Swietenia macrophylla* following the procedure reported earlier (*loc. cit.*). Homogeneous swietenine has now been prepared from their mixture first by several fractional crystallisations and subsequently by chromatography over alumina using chloroform as the eluent. Homogeneous swietenine melts at 260° (decomp.); $[\alpha]_D^{30}$, +133.5° in 4.25% chloroform solution. [Found: (in a sample dried over P_2O_5 for 4 hours): C, 67.32; H, 7.48; OMe, 6.23; : CMe, 9.15; active hydrogen, 0.38; M.W. (Rast), 310. Calc. for $C_{18}H_{24}O_5$: C, 67.5; H, 7.5; OMe, 9.69; 2 : C.Me, 9.35 : 1 active H, 0.31 per cent. M.W., 320).

Hydrolysis of Swietenine.—Swietenine (0.1134 g.) in absolute alcohol (10 c.c.) was heated on a water-bath for 1 hour with 10 c.c. of *N*/10 (approx.) NaOH with a sodalime guard tube. Swietenic acid separated from the saponified product upon careful acidification in the cold with dilute hydrochloric acid, m.p. 210° (decomp.). (Found in a dry sample: C, 63.81; H, 7.58. Calc. for $C_{18}H_{26}O_6$: C, 63.90; H, 7.70 per cent).

Formation of iso*Swietenine.*—Swietenic acid (0.1 g.) was suspended in 5 c c. of dilute HCl and heated on a water-bath for 10 minutes. It was then allowed to cool and kept in a refrigerator overnight. The brown gummy product obtained on filtration was crystallised from ethyl acetate, m.p. 262° (decomp.), yield 30 mg. It is insoluble in Na_2CO_3 solution. It reduced Tollen's reagent but not ammoniacal silver nitrate solution. [Found (in a sample dried over P_2O_5 for 4 hrs.): C, 66.71; H, 7.03; active hydrogen, 0.34; :CMe, 9.30. $C_{18}H_{24}O_6$ requires C, 67.5; H, 7.5; 1 active H, 0.31; 2 :CMe, 9.35 per cent).

Swietenine dibromide was prepared according to the method as previously described (*loc. cit.*).

Determination of Double bond in Swietenine by the Method of Winkler.—Swietenine (0.1184 g.) was dissolved in chloroform (20 c.c.). To this 25 c.c. bromine solution (3 g. $KBrO_3$ and 15 g. KBr in 1000 c.c. distilled water) and 10 c.c. of *N*-HCl were added. The mixture was shaken and allowed to stand in the dark for 2 hours. Potassium iodide solution (150 c.c., 1 g. KI in 100 c.c. distilled water) was added and the iodine liberated was titrated with 0.1 *N*-sodium thiosulphate solution.

Required 8.3 c.c. *N*/10 sodium thiosulphate solution equivalent to 0.0662 g. bromine (0.1184 g. of swietenine ≡ 0.0592 g. of bromine for addition with one double bond).

2 : 4-*Dinitrophenylhydrazone of Swietenine.*—A mixture of 2 : 4-dinitrophenylhydrazine (0.1 g.) in alcohol (10 c.c.) and HCl (conc., 2 c.c.) was heated on a water-bath when a clear solution was obtained. To this solution swietenine (0.1 g.) in acetic acid (minimum amount required to dissolve the substance) was added and then refluxed on a water-bath for ½ hour. It was then allowed to cool and kept in a refrigerator overnight when an orange crystalline precipitate appeared. It was filtered and recrystallised from alcohol as orange microcrystalline powder, m.p. 182° (decomp.). (Found in a dry sample: N, 11.35. $C_{24}H_{28}O_8N_4$ requires N, 11.2 per cent).

Pyrylium Salt of Swietenine.—A mixture of swietenine (0.1 g.) and salicylaldelyde (0.1 g.) in a mixture of chloroform and methyl alcohol (10 c.c.) was saturated with dry hydrogen chloride at 0°. The mixture which gradually became violet was left overnight in a refrigerator and then poured in ethyl alcohol containing HCl, when dark red precipitate separated. It was filtered, washed with alcohol and dried in vacuum. It did not melt up to 320°. It is soluble in hot dilute caustic soda solution imparting a red colour.

Acetylation of Swietenine.—Swietenine (0.2 g.) was dissolved in freshly distilled acetic anhydride (5 c.c.) to which 5.0 g. of fused sodium acetate was added and the mixture was kept overnight. It was then diluted with water and neutralised with $NaHCO_3$ solution. The solution was then extracted with chloroform solution after drying over anhydrous sodium sulphate, concentrated and left overnight when a brown gummy substance was obtained which failed to crystallise from any suitable solvent and even after chromatography over alumina and celite.

The acylation experiment was repeated with acetic anhydride and fused $ZnCl_2$ as also pyridine with no encouraging results.

In conclusion the authors wish to express their grateful thanks to Mrs. Chhabi Dutta, Dept. of Pure Chemistry, University College of Science, Calcutta for microanalyses. The authors further acknowledge their deep appreciation to the Government of West Bengal for financial help in this investigation.

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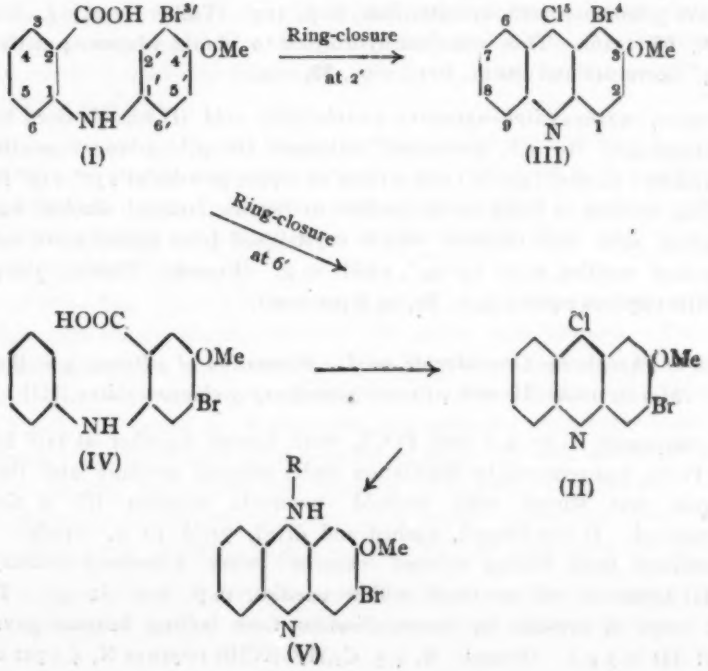
STUDIES IN ACRIDINE SERIES. PART I

By S. R. Patel and K. S. Nargund

5-(δ-Diethylamino-α-methylbutyl)-amino-2-bromo 3-methoxyacridine and other similarly N-substituted derivatives have been described. 2-Bromo-3-methoxy-5-chloroacridine has been prepared by two independent methods to prove its constitution.

The effect of bromine atom on the antimalarial activity is found to be similar to that of chlorine atom in the case of "chloroquin type" of antimalarials of the quinoline series, as chloroquin and its 7-bromo analogue have been found to have the same quinine equivalent (6) in blood-induced vivax malaria (Survey of Antimalarial Drugs, Vol. I, p. 388). Very little work has been done to study the effect of replacing the chlorine atom by a bromine atom on the antimalarial activity in the case of acridine derivatives of the atabrine type. Hence the synthesis of 2-bromo-3-methoxy-5-substituted-aminoacridine derivatives (V) was undertaken.

3-Bromo 4-methoxyaniline was condensed with *o*-chlorobenzoic acid to obtain 3′-bromo-4′-methoxydiphenylamine-2-carboxylic acid. This acid contains a substituent (Br) in 3′-position. A diphenylamine-2-carboxylic acid derivative with a substituent in 3′-position would furnish on cyclisation with $POCl_3$ two isomeric 5-chloroacridines



according as the ring-closure occurs at 2′- or 6′-position. Usually both the isomers are formed, their proportion depending on the nature of the 3′-substituent (Lehmstedt and Schrader, *Ber.*, 1937, **70**, 738; Bradbury and Linnell, *J. Chem. Soc.*, 1942, 377; Albert and Linnell, *ibid.*, 1936, 88). Hence, (I) on cyclisation with $POCl_3$ gave a mixture of two isomers: 2-bromo-3-methoxy-5-chloroacridine (II) and 4-bromo-3-methoxy-5-chloroacridine (III). They were separated by fractional crystallisation from toluene (see experimental).

In order to confirm the constitutions assigned to (II) and (III), one of them, viz., (II), was synthesised by an unambiguous method in the following manner: 2:4-Dibromo-5-methoxybenzoic acid, obtained by bromination of *m*-methoxybenzoic acid in aqueous solution, was condensed with aniline to obtain 4-methoxy-5-bromodiphenylamine-2-carboxylic acid (IV). This on cyclisation with $POCl_3$ gave 2-bromo-3-methoxy-5-chloroacridine, identical with (II) (mixed m.p.). The constitution assigned to (III) would be naturally 4-bromo-3-methoxy-5-chloroacridine. Compound (II) was then condensed with δ-diethylamino-α-methylbutylamine and other similar amino derivatives in presence of phenol (Magidson and Grigorovski, *Ber.*, 1936, **69**, 396) to obtain the corresponding 5-substituted-amino-2-bromo-3-methoxyacridines. These have been isolated as their hydrochlorides.

Experimental

3-Bromo-4-methoxyaniline.—Aceto-*p*-anisidide on bromination in acetic acid solution gave 3-bromo-4-methoxyacetanilide, m.p. 112° (Tinker *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 1546). This was then hydrolysed to obtain 3-bromo-4-methoxyaniline, m.p. 63-64° (Reverdin and Durin, *Ber.*, 1899, **32**, 162).

3′-Bromo-4′-methoxydiphenylamine-2-carboxylic acid (I) was obtained by refluxing *o*-chlorobenzoic acid (10 g.), potassium carbonate (10 g.), 3-bromo-4-methoxyaniline (13 g.), *iso*amyl alcohol (30 c.c.) and a trace of copper powder at 130°-135° for 3 hours. The resulting solution on being steam-distilled to remove *iso*amyl alcohol was acidified when a green solid was obtained which crystallised from glacial acetic acid in small greenish yellow needles, m.p. 198-99°, yield 10 g. (Found: Equiv., 320; Br, 25.0. $C_{14}H_{12}O_3NBr$ requires equiv., 322; Br, 24.8 per cent).

Action of Phosphorus Oxychloride on (I): *Formation of 2-Bromo-3-methoxy-5-chloroacridine* (II) *and 4-Bromo-3-methoxy-5-chloroacridine* (III)

The compound (I, 10 g.) and $POCl_3$ were heated together at 110° for 2 hours. Excess of $POCl_3$ was removed by distillation under reduced pressure and the resulting thick liquid was stirred with ice-cold ammonia solution till a fine yellow powder separated. It was filtered, washed and dried, yield 10 g. (crude). This was then crystallised from boiling toluene (charcoal) when 2-bromo-3-methoxy-5-chloroacridine (II) separated out as small yellow needles, m.p. 192° (2 g.). The second and third crops of crystals on recrystallisation from boiling benzene gave a further quantity of (II) (0.5 g.). (Found: N, 4.5. $C_{14}H_9ONClBr$ requires N, 4.3 per cent).

The residue obtained on evaporation of the mother-liquor was dissolved in minimum quantity of boiling benzene when a yellow crystalline solid separated out after about 2 hours. It was repeatedly crystallised from petroleum ether. The product obtained after the fourth recrystallisation was 4-bromo-3-methoxy-5-chloroacridine, m.p. 142-45°. (Found: N, 4.4. $C_{14}H_9ONClBr$ requires N, 4.3 per cent).

2 : 4-*Dibromo-5-methoxybenzoic Acid.*—Finely powdered *m*-methoxybenzoic acid (7 g.) was suspended in a solution of bromine (16 g.) in water (300 c.c.) containing sufficient potassium bromide to keep bromine in solution. It was stirred for 2 hours and left overnight. The white solid was collected and crystallised from boiling water in thin needles, m.p. 198° (Vogel, *J. prakt. Chem.*, 1913, *ii*, **88**, 330).

5-Bromo-4-methoxydiphenylamine-2-carboxylic acid was obtained by refluxing a mixture of the above compound (3.5 g.) aniline (2 c.c.), potassium carbonate (2 g.), a trace of copper powder and *iso*amyl alcohol (10 c.c.) for 3 hours at 130°-135°. It crystallised from acetic acid as a greenish crystalline solid, m.p. 198°. (Found: Equiv., 320; Br, 25.0. $C_{14}H_{12}O_3NBr$ requires equiv., 322.0; Br, 24.8 per cent).

Action of Phosphorus Oxychloride on 5-Bromo-4-methoxydiphenylamine-2-carboxylic Acid: Formation of 2-Bromo-3-methoxy-5-chloroacridine

It was obtained by refluxing a mixture of the above mentioned acid (2 g.) with $POCl_3$ (6 c.c.). It crystallised from boiling toluene in pale yellow needles, m.p. 192°; mixed m.p. with (II), described above, was undepressed.

2-Bromo-3-methoxy-5-phenoxyacridine was obtained by heating the above 5-chloroacridine (II, 1 g.) with phenol (8 c.c.) on a water-bath for 1 hour. It crystallised from alcohol in small yellow needles, m.p. 162-63°. (Found: Br, 21.4 $C_{20}H_{14}O_2NBr$ requires Br, 21.1 per cent).

2-Bromo-3-methoxy-5-(δ-diethylamino-α-methylbutyl)-aminoacridine Dihydrochloride.—2-Bromo-3-methoxy-5-chloroacridine (3 g.) was dissolved in hot phenol (12 c.c.) and δ-diethylamino-α-methylbutylamine (1.7 g.) was added to it and this mixture was heated on a water-bath for 2 hours. It was then poured after cooling in 5% ice-cold sodium hydroxide solution.

Method (1).—The thick yellow liquid which settled at the bottom was washed several times with water and extracted with 5% acetic acid solution. The acetic acid extract was decomposed with ammonia and the yellow base separating was extracted with ether. The ether extract was dried over sodium sulphate. Alcohol, saturated with HCl gas, was added to it when the hydrochloride separated out as a sticky solid which turned into a fine yellow solid in about an hour. It was dissolved in minimum quantity of alcohol and double the quantity of acetone was added to it. After about 3-4 hours the hydrochloride separated out as a yellow crystalline solid, m.p. 243-44° (decomp.), yield 1.2 g. (Found: N, 8.3. $C_{23}H_{22}ON_3Cl_2Br$ requires N, 8.1 per cent).

2-Bromo-3-methoxy-5-(γ-diethylaminopropyl)-aminoacridine dihydrochloride was obtained in the above manner from 2-bromo-3-methoxy-5-chloroacridine (1 g.), phenol

(4 g.) and γ-diethylaminopropylamine (0.6 g.). It crystallised from a mixture of alcohol and acetone (1 : 3) as a yellow crystalline powder, m.p. 238-40° (decomp.). (Found : N, 8.4. $C_{21}H_{26}ON_3Cl_2Br$ requires N, 8.5 per cent).

2-Bromo-3-methoxy-5-(γ-piperidinopropyl)-aminoacridine Hydrochloride.— γ-Piperidinopropylamine (0.6 g.) was added to a solution of 2-bromo-3-methoxy-5-chloroacridine (1 g.) in phenol (4 c.c.) and the reaction mixture was heated on a water-bath for 2 hours.

Method (II).—It was cooled and diluted with excess of dry ether and dry HCl gas was passed through it. The yellow hydrochloride separating was crystallised from alcohol-acetone mixture as a yellow crystalline solid, m.p. 248° (decomp.). (Found : N, 8.6. $C_{22}H_{28}ON_3Cl_2Br$ requires N, 8.4 per cent).

2-Bromo-3-methoxy-5-(γ-morpholinopropyl)-aminoacridine hydrochloride was obtained by Method (II) from 2-bromo-3-methoxy-5-chloroacridine (1 g.) and γ-morpholinopropylamine (0.6 g.) and phenol (4 c.c.). It crystallised from alcohol-acetone mixture as a yellow crystalline powder, m.p. 250-52° (decomp.). (Found : N, 8.5. $C_{21}H_{26}O_2N_3Cl_2Br$ requires N, 8.3 per cent).

2-Bromo-3-methoxy-5-aminoacridine hydrochloride was obtained by Method (II), using $(NH_4)_2CO_3$ as the base. It crystallised from water containing HCl in yellow light crystalline powder. It did not melt up to 300°. (Found : N, 8.4. $C_{11}H_{12}ON_2ClBr$ requires N, 8.2 per cent).

The base 2-bromo-3-methoxy-5-aminoacridine, obtained from the above hydrochloride, on treatment with alkali crystallised from alcohol in bright yellow needles, m.p. 248-50°.

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STUDIES IN LESS FAMILIAR OXIDATION STATES. PART II. ESTIMATION OF ARGENTIC OXIDE

By R. L. Dutta *

The active oxygen content of argentic oxide has been determined by oxidising ferrous ion and iodide ion in acetic acid-sodium acetate buffered medium.

Several methods are now available for the preparation of argentic oxide, AgO (Dutta, this *Journal*, 1955, **32**, 95). All earlier workers analysed the dried oxides by either thermal decomposition (Austin, *J. Chem. Soc.*, 1911, **99**, 262) or by acid decomposition using HNO_3, $HClO_4$, H_2SO_4 (Watson, *ibid.*, 1906, **89**, 578; Noyes *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 1326, Jirsa, *Chem. Listy*, 1925, **19**, 114) and collecting the evolved oxygen. Yost (*J. Amer. Chem. Soc.*, 1926, **48**, 152), Carman (*Trans. Faraday Soc.*, 1934, **30**, 566) and Barbieri and Malaguti (*Atti Accad. Lincei*, 1950, **8**, 619) have determined the ratio active O: total Ag in the freshly prepared *wet* samples by oxidising ferrous sulphate or hydrogen peroxide and then determining the total silver in the same solution. Austin (*loc.cit.*) reported erratic results while oxidising KI in sulphuric acid solution by AgO, Ag_2O_3. Jirsa (*loc.cit.*) had analysed AgO by oxidising hydrazine hydrate to nitrogen, the AgO being reduced to metallic state. He had also reported an iodimetric method, apparently without the use of any acid. Malaguti (*Chem. Abs.*, 1951, 10131) reported estimation by $FeSO_4$ or oxalic acid in H_2SO_4 solution. Yost (*loc.cit.*) and the author (*loc.cit.*) had reported earlier of the indifferent behaviour of *dried* AgO samples towards reducing agents in presence of dilute H_2SO_4.

The hydrogen peroxide and the hydrazine hydrate methods are open to doubt because any Ag_2O impurity will also be reduced to the metallic state. Again, following Jirsa, no iodine was found to be liberated unless the medium was acidic.

A further study was therefore undertaken to find out accurate methods of estimation, the modified approach being the proper control of the acidity of the medium.

Experimental

The AgO samples were all prepared by the author's hypochlorite method (*loc.cit.*) and dried over $CaCl_2$. All chemicals used were of Analar or Extrapure quality.

Ferrous Sulphate Method.—To 0.2 *N* acetic acid (40 c.c.) and 0.2 *N* sodium acetate (60 c.c.), taken in an Erlenmeyer flask, was added 25 c.c. of a standard 0.1 *N* ferrous sulphate solution (which was 0.5 *N* in H_2SO_4) and well shaken.

A weighed quantity of AgO (preferably not exceeding 0.1 g) was added to the solution and was immediately shaken till no greyish black particle was left behind undissolved. 2*N*-H_2SO_4 (35 c.c.) was then added and the excess Fe^{II} was then backtitrated

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with a standard 0.1*N*-$KMnO_4$. Premature addition of sulphuric acid was always avoided. The ferrous solution was always standardised immediately before use. Under these conditions no evolution of active oxygen of AgO was observed.

Iodimetric Method.—0.2 *N* Acetic acid (25 c.c.) and 0.2 *N* sodium acetate (25 c.c.) were pipetted into a stoppered conical flask. KI (20 g. approx.) was dissolved in this buffer solution and a weighed amount (about 0.1 g.) of AgO transfered to the solution. The flask was then swirled in subdued light till no yellowish particle was left undissolved, and then left in the dark for 5 minutes. The liberated iodine was then titrated with 0.05 *N* thiosulphate (standardised against dichromate) using starch as an indicator. The end-point was marked by the discharge of a light purple colour.

In the following table are shown results of analyses carried out according to the above procedures. For proper appreciation of these estimations, analyses done in dilute H_2SO_4 medium (using 100 c.c. of 0.2 *N*-H_2SO_4) are also included.

TABLE I

$$\%\,AgO = \frac{\text{C.c. ferrous/thio} \times \text{normality ferrous/thio} \times 0.1239 \times 100}{\text{Wt. of AgO taken}}.$$

% AgO by methods *								
I	II.	III.	I.	II.	III.	I	II.	III
Sample 1			Sample 2.			Sample 3		
81.59	98.19	98.00	72.33	90.95	91.19	80.06	97.37	97.59
83.93	98.00	98.09	68.75	90.96	91.10	77.88	97.65	97.41
73.34	98.03	97.92	...	90.86	91.23	81.50	97.46	97.34

* I-III refer respectively to $FeSO_4$ – dil. H_2SO_4, $FeSO_4$ – buffer medium and iodimetric methods.

Thus the results obtained by the methods described are in fair agreement. The ferrous sulphate method, however, has the limitation in that it does not provide good results for samples desiccated for a long time.

Attempts were made to estimate the active oxygen content of AgO by decomposing it with HCl (conc.) and absorbing the liberated chlorine in excess KI and afterwards titrating the liberated iodine with thiosulphate. This, however, gave too low values, indicating that the reaction :

$$AgO + 2HCl \longrightarrow AgCl + Cl + H_2O$$

is not quantitative and is probably accompanied by the following reactions :

$$2\,AgO + 3\,HCl \longrightarrow HOCl + H_2O + 2\,AgCl$$
$$2\,AgO + 2\,HCl \longrightarrow 2\,AgCl + H_2O + O$$

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STUDIES IN LESS FAMILIAR OXIDATION STATES. PART III. MECHANISM OF OXIDATION OF THIOSULPHATE BY ARGENTIC OXIDE

By R. L. Dutta

The oxidation of thiosulphate by argentic oxide has been studied. The reaction does not appear to be exactly stoichiometric. Analytical evidence can be explained on the basis that the primary product of oxidation is trithionate, a portion of which is further oxidised in presence of the liberated alkali to sulphate. Tetrathionate or dithionate does not appear to be formed. The above reactions are then followed by the dissolution of Ag_2O in excess thiosulphate.

Freshly prepared higher oxides of silver (Ag_2O_3 or AgO), when suspended in dilute acids, behave as strong oxidising agents. Thus they oxidise ferrous ion to ferric, manganous to MnO_2 and permanganate, chromic to chromate and iodide to iodine (Yost, *J. Amer. Chem. Soc.*, 1926, **48**, 152; Dutta, this *Journal*, 1955, **32**, 95). AgO oxidises H_2O_2 to O_2 (Barbieri and Malaguti, *Atti Accad. Lincei*, 1950, **8**, 619) and $N_2H_4.H_2O$ to N_2 (Jirsa, *Chem. Listy*, 1925, **19**, 114); these two reactions, however, are also shown by Ag_2O. Ammonia is oxidised to nitrogen but not stoichiometrically (Watson, *J. Chem. Soc.*, 1906, **89**, 578 ; Jirsa, *loc. cit.*). It appears from a search of literature that no exhaustive study of oxidation by AgO in neutral or alkaline medium has so far been made.

In this respect thiosulphate appears to be a very interesting reductant because of the solubility of silver salts in this medium. This reaction is of added interest because of the possibility of the formation of a variety of oxidation products. The work was therefore undertaken with a view to deciding the nature of the reaction and, in particular, to ascertaining the applicability of the reaction in the estimation of the active oxygen content of AgO.

Experimental

Argentic oxide, AgO, was prepared by the hypochlorite method developed by the author (*loc. cit.*) and was stored in an amber coloured bottle over $CaCl_2$. The product was analysed by the iodimetric method (Dutta, this *issue* p. 191) and was found to be 99–99.2% pure AgO. The sample being of good purity no correction in the data, recorded in the following tables, was thought necessary.

The method of estimation of the probable thio salts was based on the addition of silver nitrate to the neutral solution. The reactions :

$$Na_2S_2O_3 + 2\ AgNO_3 + H_2O \longrightarrow Ag_2S + 2NaNO_3 + H_2SO_4$$
$$Na_2S_x\ O_6 + 2AgNO_3 + 2H_2O \longrightarrow Ag_2S + (x-3)S + 2NaNO_3 + 2\ H_2SO_4$$

were found to be quantitative and the sulphate thus formed was estimated for determining the course of the reaction.

Unless otherwise mentioned, the following procedure was adopted. A weighed amount of AgO was added to a known amount of thiosulphate solution (standardised against dichromate) and shaken till dissolved. The solution was then made up to a definite volume (50 or 100 c.c.). Separate aliquots were then titrated with $N/50$-HCl in presence of phenolphthalein and also methyl orange. The difference between the two titre values (after correcting for a similar amount of thiosulphate solution) was not such as to cause any concern (sulphite absent). A neutralised portion was estimated for unchanged thiosulphate by running into excess of $N/50$ iodine solution and then backtitrating the excess iodine with $N/50$ thiosulphate (sufficient amount of KI was added to hold AgI in solution). Separate aliquots were neutralised with HCl, diluted, brought nearly to 100° and then treated with excess of $N/10$-$AgNO_3$. After filtering off the Ag_2S precipitate (which also contained AgCl) the excess $AgNO_3$ was removed by HCl; in the filtrate sulphate was determined as $BaSO_4$. The filtrate from sulphate determination was tested for dithionate, which was found to be absent.

The experimental results recorded in the following tables are all expressed in moles. The amount of $BaSO_4$ recorded in the tables was obtained after subtracting the $BaSO_4$ due to the unchanged thiosulphate from the total sulphate.

TABLE I

Oxidation of thiosulphate by* AgO.

AgO reacted.	$Na_2S_2O_3$ oxidised.	NaOH liberated.	$BaSO_4$ found.	AgO reacted.	$Na_2S_2O_3$ oxidised.	NaOH liberated.	$BaSO_4$ found.
	$Na_2S_2O_3$ added = 0.00205.				$Na_2S_2O_3$ added = 0.00410.		
0.0006	0.00016	0.00063	0.0002	0.0008	0.0022	0.00088	0.00031
0.0008	0.0002	0.00084	0.0003	0.0016	0.00043	0.00158	0.00067
0.0009	0.0002	0.00098	0.0004	0.0024	0.00060	0.00238	0.00085

* Thiosulphate used in such excess as to dissolve all the Ag_2O.

TABLE II

Immediately after the addition of the AgO, the liberated alkali was titrated with $N/10$-HCl as fast as possible. Thiosulphate was in such excess as to dissolve all the Ag_2O.

$Na_2S_2O_3$ added.	AgO reacted.	$Na_2S_2O_3$ oxidised.	NaOH liberated.	$BaSO_4$ found.
0.00205	0.00062	0.00026	0.00078	0.00034
,,	0.00081	0.00029	0.00098	0.00039
,,	0.00102	0.00035	0.00122	0.00047
0.0041	0.00162	0.00069	0.00201	0.00089
,,	0.00081	0.00034	0.00101	0.00040

TABLE III

Oxidation of alkaline thiosulphate by AgO.

NaOH added = 0.0011 *M.*

$Na_2S_2O_3$ added.	AgO reacted.	$Na_2S_2O_3$ oxidised.	NaOH liberated (corrected for added alkali).	$BaSO_4$ found.
0.0020	0.00041	0.00011	0.00041	0.00018
,,	0.00082	0.00020	0.00082	0.00031
,,	0.00105	0.00024	0.00105	0.00040
0.0041	0.00162	0.00036	0.00168	0.00057
,,	0.00120	0.00026	0.00123	0.00038

DISCUSSION

The probable reactions may now be considered in the light of the experimental procedures adopted.

Case I. If tetrathionate is the sole product of oxidation, then the reaction,

$$2\ Na_2S_2O_3 + 2\ AgO + H_2O \longrightarrow Na_2S_4O_6 + 2\ NaOH + Ag_2O \quad \ldots\ (1)$$

will be followed in presence of a large excess of thiosulphate by the reaction

$$4\ Na_2S_2O_3 + Ag_2O + H_2O \longrightarrow 2\ Na_3Ag\ (S_2O_3)_2{}^{*} + 2\ NaOH \quad \ldots\ (2)$$

These two reactions would then give $AgO : Na_2S_2O_3 : NaOH : BaSO_4$ as 8 : 8 : 16 : 8.

Case II : If trithionate is the sole product of oxidation, we have

$$3\ Na_2S_2O_3 + 8\ AgO + H_2O \longrightarrow 2\ Na_2S_3O_6 + 2\ NaOH + 4Ag_2O \quad \ldots\ (3)$$

which will be followed by (2). We would then get

$$AgO : Na_2S_2O_3 : NaOH : BaSO_4 = 8 : 3 : 10 : 4.$$

Case III : If sulphate is the sole product of oxidation, then the reaction,

$$Na_2S_2O_3 + 8\ AgO + H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + 4\ Ag_2O \quad \ldots\ (4)$$

will be followed by (2). These would then give

$$AgO : Na_2S_2O_3 : NaOH : BaSO_4 = 8 : 1 : 6 : 2.$$

From Table I the approximate mole ratios $AgO : Na_2S_2O_3 : NaOH : BaSO_4$ are found to be as 8 : 2 : 8 : 3. The AgO : NaOH ratio being 1 : 1, it may seem that the primary reaction is

$$Na_2S_2O_3 + 6\ AgO \longrightarrow Na_2S_2O_6 + 3\ Ag_2O,$$

but no dithionate is formed. Nor are the experimental results in accord with reaction (4). Then the only way of explaining the results is that the primary reaction is either (1) or (3) or both, which is then followed by a secondary reaction resulting in the removal of alkali. Considering the $AgO : Na_2S_2O_3$ ratio, the possibility of the reaction (1) occurring can be excluded. On the other hand, all these results can be explained if we assume that the primary reaction is (3), being followed by either of the following two reactions :

* There is, of course, the possibility of the formation of many other complexes, but in all cases the Ag_2O : NaOH ratio will be the same.

$$Na_2S_2O_3 + 2\ NaOH + 8\ AgO \longrightarrow 2\ Na_2SO_4 + 4\ Ag_2O + H_2O \quad \ldots\ (5)$$
$$Na_2S_3O_6 + 4\ NaOH + 8\ AgO \longrightarrow 3\ Na_2SO_4 + 4\ Ag_2O + 2H_2O \quad \ldots\ (6)$$

That the primary reaction results in the formation of trithionate is substantiated by the data in Table II. Immediately after the addition of AgO, the liberated NaOH was titrated as fast as possible with $N/10$-HCl, thus preventing any of the reactions (5) or (6) from taking place. The approximate mole ratios $AgO : Na_2S_2O_3 : NaOH : BaSO_4$ being as 8 : 3 : 10 : 4 are in complete accord with this view. Whether the secondary reaction is (5) or (6) is a question. If (5) be the actual reaction then rendering the medium alkaline, prior to the addition of AgO, would much favour the reaction. We would thus find appreciable change in the mole ratios of reactants and products as compared to those in Table I. Whereas, if (6) is the correct reaction, it would not be much influenced. Results recorded in Table III do not show any serious difference from those in Table I. We may therefore conclude that sulphate is not formed directly from thiosulphate but results from the further oxidation of the intermediate trithionate.

The Ag_2S precipitate (which also contained some AgCl) was dried at 100° and then a weighed amount was heated in an ignition tube (Bassett and Durrant, *J. Chem. Soc.*, 1927, 1451) but these showed no appreciable loss in weight. This indicated that no tetrathionate was formed in the reaction.

Complications arose while trying to oxidise thiosulphate with larger quantities of AgO because of the interaction of Ag_2O with $Na_2S_2O_3$, resulting in the formation of Ag_2S and H_2SO_4.

Behaviour of AgO towards excess of thiosulphate appears to be in line with Willstätter's observations on the oxidation of thiosulphate by H_2O_2 (Mellor, "Inorganic and Theoretical Chemistry", 1930, Vol. X, p. 496). In view of the above complications the reaction does not seem to be promising enough to be explored for the quantitative estimation of argentic oxide.

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TARTRATE COMPLEX OF TRIVALENT ANTIMONY. PART II

By K. C. Samantora, D. V. Raman Rao and S. Pani

The solubility of antimony oxide in partially neutralised tartaric acid at 35° has been determined and the p_H of the solutions measured. The equilibrium constant of the reaction for the formation of antimonyl tartrate ion from antimonyl ion and bitartrate ion has been calculated and found to be 2.44×10^4

The reaction in which antimonyl tartrate ion is formed has not been quantitatively studied. This has been investigated and the results recorded in this communication.

Experimental

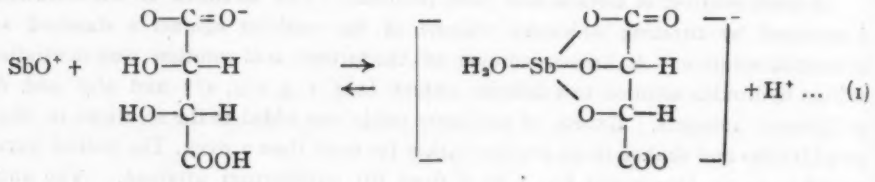
A stock solution of tartaric acid was prepared. The strength of the solution was determined by titrating a known volume of the solution against a standard sodium hydroxide solution. A known volume of the tartaric acid solution was neutralised by sodium hydroxide solution to a definite extent (1/4, 1/3, 1/2, 2/3 and 3/4) and diluted to different amounts. Excess of antimony oxide was added to the solutions in the stoppered bottles and shaken in an electric shaker for more than a week. The bottles were then placed in an air thermostat for 2 to 3 days till equilibrium attained. The antimony content and p_H' of the filtrate in each case were determined. The results are tabulated below.

Table I

Ratio of tartaric acid to sodium tartrate.	Total tartarate $[T] \times 10^3$.	Total antimony $[Sb] \times 10^3$.	Total bitartrate ion $[HT^-] \times 10^3$.	p_H.	K.
4 :3	5.0	2.400	1.445	5.17	2.18×10^4
	4.5	2.125	1.503	5.11	1.86
	4.0	1.850	1.721	5.00	1.40
	3 5	1.575	1.677	4 96	1.22
	3.0	1.425	0.7353	5.25	2.52
	2.5	1 200	0.6483	5.22	2.40
3 :2	5.0	3.250	1.314	5.03	3.21
	4 5	2 900	1.104	5.07	3.41
	4.0	2.600	0 8860	5 11	3.81
	3.5	2.300	0.7273	5.13	4 11
	3.0	1.975	0 5222	5.21	4 91
1 :1	5.0	4.400	3.566	3 65	1.60
	4 5	4 025	2 864	3.61	1.84
	3 5	3.200	1.766	3.67	2.35
	3.0	2.825	0.9694	3.77	3 78
	2.5	2.325	0 8303	3.95	3.64
3 :1	12.00	10.05	5 593	2.50	2.33
	10.67	9.025	4.719	2.50	2 48
	9 33	7.575	4.409	2.56	2.32
	8.00	6.925	3 643	2.60	2.45
	6.67	5.745	3.300	2 64	2.26
4 :1	12.10	9.675	7.930	2.30	1.59
	10.67	8.700	7.347	2.34	1.54
	9.33	7.575	6.981	2.38	1 41
	8.00	6.525	6.012	2.39	1.41
	6.67	5.475	5.552	2.46	1.29
				Mean	2.44

Discussion

In each experiment the concentration of the total tartrate [T] is a little greater than the total antimony in the solution. The solubility of antimony oxide in water being very small, it can be assumed that the whole of the antimony in the solution is present as the complex. Each antimony atom therefore cannot have more than one tartrate ligand. The solubility of antimony oxide being maximum in 50% neutralised tartaric acid solution, it is assumed that bitartarate ions react with antimonyl ion to produce antimonyl tartrate ion. The reaction may be represented by equation (1) and the equilibrium constant K is given by equation (2), where [Sb], [HT^-], [SbO^+] and [H^+] represent the molar concentrations of the complex, bitartrate ion, antimonyl ion and hydrogen ion respectively.



$$\frac{[Sb]\,[H^+]}{[SbO^+]\,[HT^-]} = K \qquad \ldots \qquad \ldots \quad (2)$$

[SbO^+] is equal to $7.7 \times 10^{-4} \times [H^+]$ (Gayer and Garrett, *J. Amer. Chem. Soc.*, 1952, **74**, 2353). Substituting this in equation (2) K is given by

$$\frac{[Sb]}{7.7 \times 10^{-4}[HT^-]} = K \qquad \ldots \qquad \ldots \quad (3)$$

The whole of the antimony in the solution is taken as the complex. The concentration of the bitartrate ion is calculated from the concentration of free tartrate (total tartarate [T] − the concentration of tartrate present in the complex [Sb]), p_H of the solution and the first and second dissociation constants of tartaric acid ($k_1 = 1.32 \times 10^{-3}$, $k_2 = 1.49 \times 10^{-4}$; Connan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314 . The values of K are shown in Table I. The mean value of K is 2.44×10^4.

It is, however, peculiar to note that in the first series of experiments the concentration of the bitartrate ion increases and then decreases with the decreasing concentration of total tartrate but similar variation in antimony content of the solutions is not observed. According to equation (3), the ratio of the concentration of the complex to the concentration of bitartrate ion should be constant. This might be due to experimental error or due to some change in the complex. This is under investigation.

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SYNTHESIS OF 2:8-DIMETHYL-3-SUBSTITUTED-QUINAZOL-4-ONES

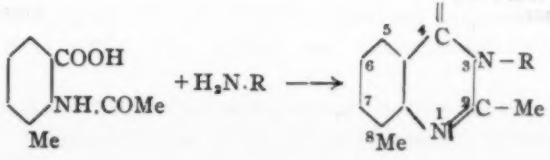
By G. S. Mewada, S. R. Patel and N. M. Shah

Several 2:8-dimethyl-3-substituted-quinazol-4-ones have been synthesised by condensation of 3-methyl-N-acetylanthranilic acid with aniline and its substituted derivatives.

Quinazolones are rare in nature; however, a few have been isolated (Koepfli, Mead and Brockmann, *J. Amer. Chem. Soc.*, 1949, **71**, 1048; Hutchings *et al.*, *J. Org. Chem.*, 1952, **17**, 19). Recently (Mrs.) D. Chakravarti and her collaborators (*J. Chem. Soc.*, 1953, 3337) isolated arborin from mature leaves of *Glycosmis arborea*, Corr., extensively used in Ayurvedic medicine as febrifuge and anthelmintic, and proved it synthetically to be a quinazolone derivative. Chatterjee and Ghosh Majmudar (*J. Amer. Chem. Soc.*, 1954, **76**, 2450) have obtained from *Glycosmis pentaphylla* (Retz) DC. three alkaloids, one of which has been proved to be a quinazolone derivative, probably identical with arborin. In order to ascertain the possibility of other quinazolones possessing such medicinal properties, the present work has been undertaken and several hitherto unknown quinazol-4-ones are reported in this paper.

Of the various synthetic methods (Korner, *J. prakt. Chem.*, 1887, *ii*, **36**, 165; Bogert *et al.*, *J. Amer. Chem. Soc.*, 1900, **22**, 534; 1905, **27**, 649; 1909, **31**, 512; McKee and Bost, *ibid.*, 1947, **69**, 940; Anscutz, Schmidt and Griffenberg, *Ber.*, 1902, **35**, 3482) that of Grimmel, Guenther and Morgan (*J. Amer. Chem. Soc.*, 1946, **68**, 542) is extremely convenient as it can be carried out at a moderate temperature using N-acylanthranilic acid as the starting material. Several quinazol-4-ones have been thus prepared (Rani, Vig, Gupta and Narang, this *Journal*, 1953, **30**, 331; Subbaram, *Proc. Ind. Acad. Sci.*, 1954, **40A**, 22). As an alkyl group imparts more solubility to organic compounds in lipoids, attempts have been made to synthesise hitherto unknown alkylated quinazol-4-ones from 3-methyl-N-acetylanthranilic acid.

3-Methyl-N-acetylanthranilic acid required for this work was prepared by oxidation of 7-methylisatin, followed by acetylation of 3-methylanthranilic acid obtained with acetic anhydride in benzene (Miller and Meyer, *Ber.*, 1891, **A 24**, 1909). The N-acyl acid, suspended in dry toluene was then treated with different amines, viz, aniline, *p*-anisidine, *o*- and *p*-toluidines, *o*- and *p*-chloro- and nitro-anilines, in presence of phosphorus trichloride when 2:8-dimethyl-3-arylquinazol-4-ones were obtained in good yields.



EXPERIMENTAL

General Method of Preparation.—All the quinazol-4-ones, described in this paper, were prepared by condensing 3-methyl-N-acetyanthranilic acid (1 g., 1 mol.) with different amines (1 mol.), suspended in dry toluene (30 ml.) in presence of PCl_3 (0.5 ml. dissolved in 5 ml. of dry toluene). The reaction was carried out in a three-necked flask equipped with a mechanical stirrer, reflux condenser and a dropping funnel from which the solution of PCl_3 was added dropwise during the first five minutes with constant stirring, when a thick white solid separated out. The resulting suspension was then refluxed in an oil-bath at 130°-135° for 2 hours with stirring. A pale yellow pasty mass separated out. After cooling, it was treated with sodium carbonate solution (10%, 100 ml.) when it solidified. The reaction mixture was then subjected to steam-distillation. After removal of the toluene, the residue was collected and crystallised from dilute alcohol (80%), yield 70-80%. It was then recrystallised from petroleum ether (b.p. 80°-100°).

The hydrochlorides of the above quinazol-4-ones were prepared by dissolving the base in alcohol and adding a few drops of HCl (conc.). Their equivalents were determined by titrating against a standard alkali. Except in case of I and II, the hydrochlorides could not be obtained. The 2:8-dimethyl-3-R-quinazol-4-ones, prepared, are tabulated below.

TABLE I.

	R.	M. P.	Crystalline form.	Formula	Analysis. Found.	Calc.
I.	$-C_6H_5$	148°	Short needles	$C_{16}H_{14}ON_2$	N, 11.4 %	11.2 %
	Hydrochloride of (I)	212° (decomp.)	Needles	$C_{16}H_{15}ON_2Cl$	Equiv. 281	286
II.	$-C_6H_4-OCH_3$ (*p*)	135°	Rhombic crystals	$C_{17}H_{16}O_2N_2$	N, 10.2	10.0
	Hydrochloride of (II)	220° (decomp.)	Lustrous needles	$C_{17}H_{17}O_2N_2Cl$	Equiv. 312	31.6
III.	$-C_6H_4-CH_3$ (*o*)	140°	Stout needles	$C_{17}H_{16}ON_2$	N, 10.7	10.6
IV.	$-C_6H_4-CH_3$ (*p*)	140°	Feathery plates	$C_{17}H_{16}ON_2$	N 10.8	10.6
V.	$-C_6H_4-Cl$ (*o*)	150°	Lustrous plates	$C_{16}H_{13}ON_2Cl$	N, 10.1	9.8
					Cl, 12.8	12.5
VI.	$-C_6H_4-Cl$ (*p*)	151°	Rhombic needles	$C_{16}H_{13}ON_2Cl$	N, 10.0	9.8
					Cl, 12.7	12.5
VII.	$-C_6H_4-NO_2$ (*o*)	195°	Reddish yellow needles	$C_{16}H_{13}O_3N_3$	N, 14.1	14.2
VIII.	$C_6H_4-NO_2$ (*p*)	197°	Yellowish needles	$C_{16}H_{13}O_3N_3$	N, 14.4	14.2

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NOTE ON THE CROSSED CANNIZZARO REACTION

By G. S. Misra and S. B. Srivastava

It was observed by Nenitzescu and Gavat (*Bul. Soc. Chim. Romaina*, 1934, **16A**, 42) that when an equimolecular mixture of an aromatic aldehyde, like benzaldehyde, and formaldehyde was submitted to the Cannizzaro reaction, both possible acids and alcohols were formed. If, however, formaldehyde was present in excess, the aromatic alcohol was obtained in a very good yield. This method thus furnishes a practical mean for the preparation of an aromatic alcohol from the corresponding aldehyde. Davidson and Bogert (*J. Amer. Chem. Soc.*, 1935, **57**, 905) worked out the experimental conditions for this reaction and obatined the alcohols from the corresponding aldehydes in yields of 85-90%. Thus, anisaldehyde, veratraldehyde, piperonaldehyde, opianic acid, phthalaldehydic acid and furfuraldehyde undergo the reduction smoothly. *p-iso*Propylbenzaldehyde, however, furnishes a yield of only 42% (Cooke, Gillespie and Macbeth, *J. Chem. Soc.*, 1938, 1825). *m*-Nitrobenzaldehyde (Nenitzescu and Gavat, *loc. cit.*) and *p*-phenylbenzaldehyde were not found to undergo this reaction.

The present study was undertaken to find out the effect of different structural modifications upon the ease with which the crossed reaction took place. It was found that with 100% aqueous NaOH and one hour reaction time, *o*-, *m*- and *p*-chloro-, *o*- and *m*- methoxy-, *o*-methyl-, *o*-, *m*- and *p*-nitro-benzaldehydes underwent the crossed Cannizzaro reaction, to furnish alcohols in yields of 50-90%; *o*- and *p*-hydroxybenzaldehyde, *p*- dimethylaminobenzaldehyde and *p*-acetylaminobenzaldehyde were not found to undergo this reaction at all. By decreasing the concentration of the NaOH solution to 50% and increasing the reaction time to two hours, these did not undergo the reduction. In a few other cases examined, the yields registered a decrease.

o-Chlorobenzyl Alcohol.—Into a 250 c.c. three-necked flask, fitted with a mercury sealed mechanical stirrer, a dropping funnel and a condenser, were introduced *o*-chlorobenzaldehyde (10 g.), methanol (7.5 c.c.) and formalin (3 6 c.c.). The mixture was heated to 65° and then surrounded by cold water. Immediately a solution of caustic soda (4.5 g.) in water (4.5 c.c) was run into the reaction mixture. This was then heated at 70° for 40 minutes and then refluxed for 20 minutes. After this, the reaction mixture was cooled and diluted with water. The alcohol separated as a white solid. It was filtered, dried and recrystallised from alcohol, m.p. 70° (*lit.* m.p. 69.5°-72°), yield 9 g.(90%).

The experiment was repeated with 50% NaOH solution and two hours as the reaction time. Yield decreased to 10%. The alcohol was characterised by preparing its 3 : 5-dinitrobenzoate.

m-*Chlorobenzyl Alcohol.*—The alcohol was prepared in the same way as above with m-chlorobenzaldehyde. It separated as an oil on cooling the reaction mixture and diluting it with water. The oil was separated as far as possible from the aqueous layer. The

aqueous layer was further extracted with benzene. The combined oil and the extract was washed with water several times and dried over anhydrous sodium sulphate. Benzene was then removed under reduced pressure and the alcohol distilled in vacuum. The fraction, b.p. 104°-106°/13 mm. was collected, yield 70%. The alcohol was characterised by preparing its 3:5-dinitrobenzoate.

TABLE I

Substituted aldehyde.	Alcohol formed.	Yield with Aq. NaOH 100% & 1 hr.	50% & 2 hrs. reaction time.	M.P. or B.P.		3:5-Dinitrobenzoate.			
(R.C_6H_4.CHO)	(R.C_6H_4.CH_2OH)			Found.	Lit.	M. P.	Mol. fomulla.	% Nitrogen. Found.	Calc
R=	R=								
o-Chloro-	*o*-Chloro-	90%	10%	70°	69.5°-70°	126°	$C_{14}H_9O_6N_2Cl$	8.46	8.33
m- ,,	*m*- ,,	70	...	104°-106°/13 mm.	234°/760 mm.	84°	$C_{14}H_9O_6N_2Cl$	8.22	8.33
p- ,,	*p*- ,,	92	14	71°	70.5°-73°	86°	$C_{14}H_9O_6N_2Cl$	8.51	8.33
o-Methoxy-	*o*-Methoxy-	73	...	140°-145°/20	247°/765	100°	$C_{15}H_{12}O_7N_2$	8.30	8.43
m- ,,	*m*- ,,	79	...	145°-150°/20	252°/760	93°	$C_{15}H_{12}O_7N_2$	8.35	8.43
o-Nitro-	*o*-Nitro-	50	50	72°	74°	94°	$C_{14}H_8O_8N_2$	11.90	12.10
m- ,,	*m*- ,,	50	50	165°-170°/13	175°-180°/3	84°	$C_{14}H_8O_8N_2$	12.30	12.10
p- ,,	*p*- ,,	52	...	93°	93°	90°	$C_{14}H_8O_8N_2$	12.25	12.10
o-Methyl-	*o*-Methyl-	66	...	101°-103°/13	223°/750	85°	$C_{15}H_{12}O_6N_2$	9.10	8.86

Table I records the yields of alcohols obtained from various aldehydes.

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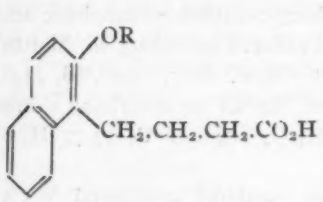
4

SYNTHESIS OF 6:7-BENZOHOMOCHROMAN

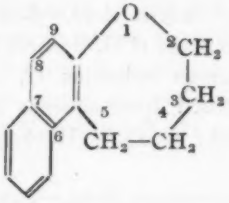
By J. N. Chatterjea

A systhesis of the compound named in the title is reported.

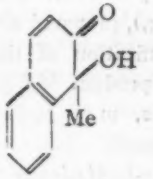
Homochromanone was first described by Powell and Anderson (*J. Amer. Chem. Soc.*, 1931, **53**, 811). The ring system present in this compound appears to have been described first by Sen and Roy (this *Journal*, 1930, **7**, 743). Cagniant has developed the synthesis of the homochromans and their related derivatives (*Compt. rend.*, 1949, **229**, 889; cf. *ibid.*, 1946, **223**, 677). In view of the recent exhaustive work on this class of compounds by Dann and Arndt (*Annalen*, 1954, **587**, 38), it is desirable to report the synthesis of 6:7-benzohomochroman (II). This synthesis was effected in this laboratory some years back.



(I)



(II)

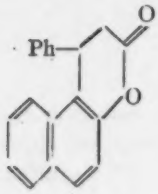


(III)

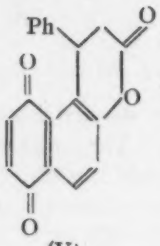
β-(2-Methoxy-1-naphthoylpropionic acid), which was prepared according to Short *et al.* (*J. Chem. Soc.*, 1936, 319) by the action of succinic anhydride on 2-methoxynaphthalene in carbon disulphide, was reduced by the Clemmensen -Martin procedure to γ-(2-methoxy-1-naphthyl)-butyric acid (I, R = Me). This on demethylation by hydrobromic acid in acetic acid furnished (I, R = H), described earlier by Shroeter (*Ber.*, 1930, **63**, 1328) who used a different method. Reduction of this acid to the corresponding alcohol was brought about by lithium aluminium hydride in about 90% yield (cf. Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548). Cyclisation of the resulting dihydroxy compound (I, R = H and CH_2OH in place of COOH) with hydrogen bromide in acetic acid afforded 6:7-benzohomochroman (II).

A few experiments were carried out to oxidise the phenolic acid (I, R=H) to the corresponding dehydro compound (cf. Chatterjea, this *Journal*, 1950, **27**, 375). Bargellini and Silvestri (*Gazzetta*, 1907, **37**, 412) had obtained the αβ-unsaturated ketone (III) from 1-methyl-2-naphthol by oxidation with chromic acid. Woodward and Doering (*J. Amer. Chem. Soc.*, 1954, **67**, 863) obtained (III) by employing peracetic acid, and also Koelsch (*ibid.*, 1936, **58**, 1326) reported similar oxidation products. In the present case, the oxidation experiments with (I, R=H) did not proceed at all in the desired way. Oxidation with alkaline hypochlorites, hydrogen peroxide in acetic or formic acid or with ferric chloride was not possible, unchanged material having been obtained

in each case. Analogous experiments were also tried on 3:4-dihydro-4-phenyl-5:6-benzocoumarin (IV) (Koelsch, *loc. cit.*). This compound remained unchanged with mild oxidising agents in alkaline solution, while chromic acid in acetic acid oxidised the material smoothly to the quinone (V).



(IV)



(V)

EXPERIMENTAL

(All m.p.'s are uncorrected).

γ-(2-*Methoxy*-1-*naphthyl*)-*butyric Acid*.—β-(2-Methoxy-1-naphthoyl-propionic acid) (10 g.), prepared according to Short *et al.* (*loc. cit.*), was reduced according to Martin's modification of the Clemmensen reduction (*J. Amer. Chem. Soc.*, 1936, **58**, 1438). The product (6.6 g.) crystallised from aqueous alcohol (60 %) in colorless, shining plates, m.p. 79-81°. (Found: C, 73.6; H, 6.4. $C_{15}H_{16}O_3$ requires C, 73.7; H, 6.5 per cent).

γ-(2-*Hydroxy*-1-*naphthyl*)-*butyric Acid*.—The above methoxy compound (0.5 g.) in acetic acid (15 c.c.) was boiled under reflux with hydrobromic acid (30 c.c., 48%). The product was isolated by pouring the solution into water. The compound crystallised from dilute alcohol or dilute acetic acid in prisms (0.35 g.) which melted over a long range due to occlusion of solvents. From benzene it was obtained in colorless plates, m.p. 136-37° (Shroeter, m.p. 136-37°). (Found: C, 73.4; H, 6.0. Calc. for $C_{14}H_{14}O_3$: C, 73.1; H, 6.1 per cent).

6:7-*Benzohomochroman*.—The foregoing acid (1.0 g.) in ether (30 c.c., dried over sodium) was added to a cooled slurry of lithium aluminium hydride (0.85 g.) in ether (30 c.c.). A vigorous reaction took place and the mixture was stirred and maintained at 20° for 72 hours. The excess of the hydride was decomposed carefully with water, acidified with dilute hydrochloric acid and the ethereal layer washed successively with water, sodium bicarbonate solution and then extracted with dilute alkali. The sodium bicarbonate washings on acidification afforded no unchanged acid. The violet fluorescing alkaline solution was acidified yielding the dihydroxy compound (I, R = H and CH_2OH in place of COOH) as an oil which was isolated with ether and dried in vacuum, yield 0.85 g.

Cyclisation.—The foregoing alcohol was dissolved in anhydrous acetic acid (5 c.c.) and saturated with dry hydrogen bromide, and the dark mixture was left overnight. Next day, the whole mass was basified with aqueous NaOH and warmed on the water-bath for 2 hours. The insoluble oil was extracted with ether, dried over potassium hydroxide and the residue after removal of the ether distilled in vacuum. 6:7-*Benzo-*

homochroman was obtained as a colorless oil (0.13 g.), b.p. 179-82°./2 mm. (bath temp.). (Found: C, 84.5; H, 7.4. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1 per cent).

The product has a slightly aromatic odour; it decolorises permanganate and bromine in the cold. With sulphuric acid it gives a yellow solution which turns leafy green gradually.

Infra-red absorption spectrum (in chloroform): $\lambda_{max.}$ 3.39, 6.05, 6.26, 6.39, 6.62, 6.78,6.88,7.18; (-CH_2-deformation), 8.1 (ether), 9.68, 10.14, 12.24μ.

Oxidation of 3:4-Dihydro-4-phenyl-5:6-benzocoumarin with Chromic Acid.—The dihydrocoumarin (IV, 1.0 g.), prepared according to Koelsch (*loc. cit.*), in acetic acid (15 c.c.) was treated with chromic acid (2.0 g.) in dilute acetic acid. The temperature was kept below 50° by cooling. After leaving for it 2 hours at the ordinary temperature, the mixture was poured into water and extracted repeatedly with ether. After washing with dilute sodium carbonate, the ethereal solution furnished a neutral product (0.4 g.) crystallising from alcohol in bright yellow plates, m.p. 185° (previous sintering) and analysed as the *quinone* (V). (Found: C, 74.5; H, 4.1. $C_{19}H_{12}O_4$ requires C, 75.0; H, 3.9 per cent). The product is insoluble in cold alkali; on warming a dirty brown solution is obtained. It dissolves in concentrated sulphuric acid, forming a yellow solution exhibiting an intense green fluorescence.

With 2:4-dinitrophenylhydrazine it gave a *hydroxy-azo* derivative (*mono*-2:4-dinitrophenylhydrazone), crystallising from acetic acid in orange-red plates, m.p. 277° (decomp.). (Found: N, 11.0. $C_{25}H_{16}O_7N_4$ requires N, 11.5 per cent).

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CHALKONES. PART IV. BROMINATION OF 2-HYDROXY-4-BENZYLOXY-5-NITROCHALKONE

By (Miss) Fatima A. Atchabba, P. L. Trivedi and G. V. Jadhav

2-Hydroxy-4-benzyloxy-5-nitrophenylstyryl ketone was brominated with one or more moles of bromine in chloroform solution and with liquid bromine, affording 2-hydroxy-4-benzyloxy-5-nitrophenyl-αβ-dibromo-β-phenylethyl ketone and 2 :4-dihydroxy-3-bromo-5-nitrophenyl-αβ-dibromo-β-phenylethyl ketone respectively.

The reactivity of the dibromide has also been studied with dimethylaniline, pyridine, borax, sodium carbonate, potassium cyanide and caustic potash, and in all cases 7-benzyloxy-6-nitroflavone has been obtained.

The present work was taken up with a view to studying the effect of substitution of the hydrogen of the hydroxy group in 4-position of 2:4-dihydroxy-5-nitrochalkone with a heavier group like benzyl, as Kulkarni and Jadhav (this *Journal*, 1954, **31**, 746 ; 1955, **32**, 97) have observed that mere substitution of H of this hydroxyl group by Me changes the course of the reaction in the case of bromination. In the simple 2:4-dihydroxy-5-nitrochalkone, bromine was found to enter first in the ketonic nucleus, whereas in the case of its 4-methoxy derivative no bromine entered the ketonic nucleus. In the present work also, no bromine enters the ketonic nucleus under those conditions even though the Me group has been replaced by the benzyloxy group. The reactivity of the dibromide of the benzyloxychalkone derivative differs a great deal from the reactivity of the dibromides of the two chalkones referred to above (*loc. cit.*).

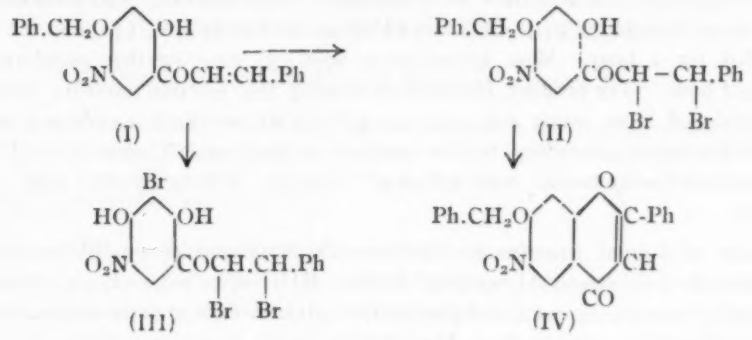
2-Hydroxy-4-benzyloxy-5-nitrophenylstyryl ketone (I) was prepared according to the method of Sorge (*Ber.*, 1902, **35**, 1069). Bromination of the chalkone in chloroform solution with one or more moles of bromine gave 2-hydroxy-4-benzyloxy-5-nitrophenyl-αβ-dibromo-β-phenylethyl ketone (II). The constitution of the product was arrived at by potassium iodide reaction, which regenerated the original chalkone (I).

With liquid bromine in the present case, bromine not only adds on at the double bond but also substitutes hydrogen in 3-position of the ketonic nucleus, and subsequently debenzylation takes place due to the action of hydrogen bromide generated in the above substitution, the product obtained being 2:4-dihydroxy-3-bromo-5-nitrophenyl-αβ-dibromo-β-phenylethyl ketone (III).

With pyridine, caustic potash, potassium cyanide, borax, sodium carbonate and dimethylaniline, the dibromide (II) gave 7-benzyloxy-6-nitroflavone (IV). This shows that the entry of a heavier group in place of a lighter one greatly influences the course of the reaction.

The constitution of the flavone (IV) was arrived at by debenzylating it, when 7-hydroxy-6-nitroflavone was obtained, whose melting point agreed with that of the flavone prepared by Naik and Thakor (*Proc. Ind. Acad. Sci.*, 1953, **37A**, 780). As this flavone could not be synthesised due to its formation in a very poor yield in the reaction of the above authors, to confirm the constitution of the flavone obained, its further

nitration was carried out. The melting point of the nitration product agreed with that of 7-hydroxy-6:8-dinitroflavone. Its constitution was confirmed by taking mixed melting point with an authentic specimen of 7-hydroxy-6:8-dinitroflavone (Mehta Jadhav and Shah, *ibid.*, 1949, **29A**, 314).



EXPERIMENTAL

2-Hydroxy-4-benzyloxy-5-nitrophenylstyryl Ketone (I).—2-Hydroxy-4-benzyloxy-5-nitroacetophenone (5 g.), benzaldehyde (4 c.c.), alcohol (20 c.c.) and KOH (50 g. in 50 c.c. of H_2O) were mixed together and left at room temperature for 7 days with occasional shaking or were constantly shaken for a day. The mixture was then diluted, acidified with HCl and the product obtained was finally crystallised from acetic acid in yellow needles, m.p. 204°. (Found: C, 70.2 ; H, 4.2. $C_{22}H_{17}O_5N$ requires C, 70.4 ; H, 4.5 per cent).

2-Hydroxy-4-benzyloxy-5-nitrophenyl-αβ-dibromo-β-phenylethyl Ketone (II).—Chalkone (I, 1 g.) was dissolved in chloroform (40 c.c.) and 40% solution of bromine (3.3 c.c.) in chloroform was added to it. The reaction mixture was heated on a water-bath for about 3 hours. The product obtained after removal of the chloroform was crystallised from acetic acid in white needles, m.p. 204°. (Found : Br, 30.15. $C_{22}H_{17}O_5NBr_2$ requires Br, 29.9 per cent).

Chalkone dibromide (II, 1 g.) was dissolved in acetone (40 c.c.) and KI was added to it. The mixture was heated on a boiling water-bath for about 45 minutes. Sodium thiosulphate solution was then added to it to remove the liberated iodine. The product left over on removal of acetone was crystallised from acetic acid, m.p. 204°. It was found to be identical with (I) by mixed melting point.

Action of Pyridine on Chalkone Dibromide (II): *Formation of 7-Benzyloxy-6-nitroflavone* (IV).—Chalkone dibromide (II, 1 g.) was boiled with pyridine (5 c.c.) for about ten minutes, diluted with water, acidified with HCl, and the product separating was crystallised from acetic acid in faint yellow shining plates, m.p. 265°. (Found: C, 70.3; H, 4.17. $C_{22}H_{15}O_5N$ requires C, 70.8 ; H, 4.02 per cent).

The flavone (IV) was also obtained from chalkone dibromide (II, 1.g) when it was boiled (*i*) with 10% KOH solution (40 c.c.) for about 2 hours, (*ii*) for 45 minutes with KCN (1.g in 20 c.c. of alcohol and 5 c.c. of H_2O), (*iii*) for 4 hours with dimethyl-

aniline (10 c.c.) in presence of alcohol (30 c.c.), (*iv*) for 4 hours with borax (3 g in 15 c.c. of H_2O) in presence of alcohol (30 c.c.) and (*v*) with 10% solution of sodium carbonate (20 c.c.) for about an hour and then diluting and acidifying the solution in all cases.

Debenzylation and Nitration of *7-Benzyloxy-6-nitroflavone*.—Hydrobromic acid solution in acetic acid (30%, 50 c.c.) was added to the flavone (IV, 1 g.) and the mixture was boiled for 1 hour. More hydrobromic acid (50 c.c.) was then added and boiled for another hour. The product, obtained on pouring the reaction mixture into water, was crystallised from acetic acid, m.p. 230-32° (Naik and Thakor gave m.p. 230-33°). It was then nitrated according to the method of Naik and Thakor (*loc. cit.*) when 7-hydroxy-6:8-dinitroflavone was obtained (mixed melting point with genuine specimen).

Action of Liquid Bromine on Chalkone (I) : *Formation of 2:4-Dihyroxy-3-bromo-5-nitrophenyl-αβ-dibromo-β-phenylethyl Ketone* (III).—Chalkone (I, 1 g.) was mixed with liquid bromine (2 c.c.) and the solution left overnight at room temperature. On dilution and washing with sodium bisulphite a pasty mass was obtained, which on trituration with acetic acid turned into a solid. It was crystallised from acetic acid in tiny white needles, m.p. 225°. (Found : Br, 45.54. Calc. for $C_{15}H_{10}O_5NBr_3$: Br, 45.8 per cent).

It was found to be identical with 2:4 -dihydroxy-3-bromo-5-nitrophenyl-αβ-dibromo-β-phenylethyl ketone (Kulkarni and Jadhav, *loc. cit.*) by mixed melting point.

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Errata

In Part III of this series in the February issue, 1955, the following misprints require rectification.

Page	Line.	Read.	For.
98	Table I, Column 7, line 1	$C_{16}H_{13}O_5N$	$C_6H_{13}O_5N$
99	Table III, ,, 6, last line	$C_{11}H_{11}O_6N$	$C_{17}H_{13}ON$
100	Table IV, ,, 5, line 6	264–65°	254–65°

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FLUOBERYLLATES AND THEIR ANALOGY WITH SULPHATES. PART XI. COMPLEX COMPOUNDS OF FLUOBERYLLATES WITH ETHYLENE- AND PROPYLENE-DIAMINES

By Amiya Kanti Ghosh and Nirmalendunath Ray

Complex compounds of copper and nickel fluoberyllates with ethylenediamine and propylenediamine have been prepared. The compounds are analogous in chemical composition and properties to similar complex compounds formed with sulphates of Ni and Cu. The results adduce further proof to the analogy of fluoberyllates with sulphates.

Organic diamines such as ethylenediamine, propylenediamine, etc. form remarkably stable chelate compounds with metals. With trivalent elements such as chromium and cobalt, Werner prepared a large number of stable compounds of the type $[M(en)_3]X_3$. Werner *et al.* (*Z. anorg. Chem.*, 1899, **21**, 201) prepared a large number of complex compounds of ethylenediamine (en) and propylenediamine (pn) with sulphates of bivalent metals, e.g., $[Cu\ en_2(H_2O)_2]SO_4$; $[Cu\ en_3]SO_4$; $[Ni\ en_3]SO_4$; $[Co\ en_3]SO_4$, $[Zn\ en_3]SO_4$; $[Cd\ en_3]SO_4$; $[Ni\ pn_3]SO_4$ etc.

In view of the close analogy between fluoberyllates and sulphates, it was expected that fluoberyllates should also form similar complex compounds with ethylenediamine and propylenediamine. The present paper deals with the preparation and properties of such complex compounds of copper and nickel fluoberyllates.

Experimental

Ethylenediamine Complexes

Diethylenediamine-copper Fluoberyllate Tetrahydrate.—To a cold saturated solution of copper fluoberyllate, 10-15% solution of ethylenediamine in water was slowly added. As the addition of ethylenediamine solution continued, a precipitate was formed which went into solution readily. The mixture was cooled by ice and salt. The addition of ethylenediamine was continued till the solution was perfectly blue. The solution was filtered and the filtrate was kept in vacuum over H_2SO_4. In two or three days deep blue crystals were obtained. The crystals were filtered, washed with alcohol, dried in air and analysed. The crystals are soluble in water and stable in air. {Found: Cu, 18.54 ; Be, 2.80 ; N, 16.67. $[Cu\ en_2]\ BeF_4, 4H_2O$ requires Cu, 18.67 ; Be, 2.78 ; N, 16.44 per cent}.

Triethylendiamine-copper Fluoberyllate.—To a cold saturated solution of copper fluoberyllate anhydrous ethylenediamine was slowly added and the mixture was cooled. The colour of the solution gradually changed to deep blue and finally to pink. Further addition of ethylenediamine caused precipitation, which did not easily go into solution even on prolonged cooling in ice and salt mixture. The solution was filtered and crystallised in the same way as in the previous compound. The crystals

were washed, dried and analysed. The substance forms bluish pink crystals, soluble in water and stable in air. {Found: Cu, 19.2; Be, 2.67; en, 55.09. [Cu en_3] BeF_4 requires Cu, 19.35; Be, 2.74; en, 54.78 per cent}.

Triethylenediamine-copper fluoberyllate trihydrate was prepared in the same way as the anhydrous compound, using ethylenediamine monohydrate (100%) in place of anhydrous ethylenediamine. The compound is deep bluish pink. It was filtered, washed, and dried as before and analysed. {Found: Cu, 16.7; N, 21.47. [Cu en_3] BeF_4, $3H_2O$ requires Cu, 16.6; N, 21.86 per cent}.

Triethylenediamine-nickel Fluoberyllate.—Ethylenediamine monohydrate (12-15% soln. by vol.) was added slowly to a concentrated solution of nickel fluoberyllate, and kept in an ice-bath. The ethylenediamine was added until the green solution became perfectly pink-violet and no further colour change took place. The solution was filtered and the filtrate kept in a vacuum desiccator over H_2SO_4 for a few days. The crystals obtained were washed and dried in the usual way. The crystals are violet in colour, stable and soluble in water. {Found: Ni, 17.95; Be, 2.59; N, 25.75. [Ni en_3] BeF_4 requires Ni, 18.08; Be, 2.78; N, 25.96 per cent}.

An attempt to prepare the compound [Ni en_3]BeF_4,2KI, analogous to $[Ni(NH_3)_6]SO_4$, 2KI, was not successful. The compound obtained on analysis showed a slight excess of beryllium than the calculated formula due to partial decomposition of the $[BeF_4]^{2-}$ ion.

Propylenediamine Complexes

Tripropylenediamine-copper fluoberyllate trihydrate was prepared in the cold in the same way as that used in the preparation of the corresponding triethylenediamine copper compound using 5.7 g. of $CuBeF_4$, $5H_2O$ and about 9 c.c. of 70% propylenediamine solution. The compound is bluish pink, soluble in water and stable. It was washed with alcohol, dried and analysed. {Found: Cu, 14.97; Be, 2.11. [Cu pn_3] BeF_4, $3H_2O$ requires Cu, 15.3; Be, 2.17 per cent}.

Tripropylenediamine - nickel fluoberyllate was prepared in the same way as that used in the preparation of triethylenediamine-nickel fluoberyllate using 5.4 g. of $NiBeF_4$, $7H_2O$ and 6.5 c.c. of a 70% solution of propylenediamine. The compound is pink, soluble in water and stable. It was washed with alcohol, dried and analysed. {Found: Ni, 16.23; Be, 2.47; N, 23.2. [Ni pn_3] BeF_4 requires Ni, 16.03; Be, 2.46; N, 22.98 per cent}.

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BOILING POINT ADDITIVE FUNCTION FOR METHANE AND SILANE DERIVATIVES

By Yatendra Pal Varshni and Hari Mohan

A simple and satisfactory additive scheme has been proposed for the various methane and silane derivatives with regard to their boiling points, considering that the additive function (T_b^2) incorporates contributions from the interaction between non-bonded atoms besides the contributions due to bonded atoms.

Additive functions depending on boiling points (T_b), critical constants etc. have been proposed and investigated by several workers (Burnop, *J. Chem. Soc.*, 1938, 826, 1614; Kinney, *J. Amer. Chem. Soc.*, 1938, **60**, 3032; 1939, **61**, 3236; Klages, *Ber.*, 1943, **76**, 788; Grunberg and Nissan, *Trans. Faraday Soc.*, 1948, **44**, 1013; Thomas, *J. Chem. Soc.*, 1949, 3411; Riedel, *Chem. Ing. Tech.*, 1952, **6**, 353; Varshni, *Curr. Sci.*, 1953, **22**, 140; Varshni and Srivastava, *Science & Culture*, 1953, **19**, 308; Mitra, *J. Chem. Phys.*, 1954, **22**, 150; Lewis and Newkirk, *J. Amer. Chem. Soc.*, 1947, **69**, 701; Varshni, *Naturwis.*, 1953, **40**, 622; *Z. physikal. Chem.*, 1954, **203**, 247; Mitra and Varshni, *J. Phys. Chem.*, 1954, **58**, 381). A detailed discussion on boiling points may be had from Partington ("An Advanced Treatise on Physical Chemistry, Properties of Liquids", Longmans Green & Co., 1951).

One of the simplest additive function which has been investigated is T_b^2. This follows from the empirical formula due to Boggio-Lera (*Gazzetta*, 1899, **29**, 441).

$$T^b = A(M+B)^{\frac{1}{2}}$$

where M is the molecular weight and A and B are constants. Formulae involving $M^{1/2}$ were also proposed by Sugden (*Chem. News*, 1913, **107**, 135), Nikiforov (*J. Phys. Chem., U.S.S.R.*, 1937, **9**, 449, 454) etc. Aten (*J. Chem. Phys.*, 1937, **5**, 260, 264) has provided a semi-theoretical support to such formulae. The function T_b^2 has been investigated in detail by Klages (*loc. cit.*). There is a slight decrease in the additivity value as we ascend the normal paraffins (Varshni, this *Journal*, 1951, **28**, 535, formula II); however, for the corresponding members of monohalogen derivatives and the normal paraffins, the difference ($T^2_{hal} - T^2_{par}$) is constant to a good degree (Varshni, this *Journal*, 1953, **30**, 169).

For a satisfactory additive function, the change (increase or decrease) in its value with each addition or subtraction of a particular group should be constant. Thus, in the chain,

$$CH_4 \longrightarrow CH_3X \longrightarrow CH_2X_2 \longrightarrow CHX_3 \longrightarrow CX_4$$

for each step, there should be equal changes in the additive function. For most of the additive functions, while it is true for (CH_2) group, it fails for Cl, Br, I, etc. This is illustrated for T_b^2 in Table I. The values are in units of 10^3 (degrees)^2.

TABLE I

	CH_4.	Diff.	CH_3X.	Diff.	CH_2X_2.	Diff.	CHX_3.	Diff.	CX_4
F	12.43	25 37	37.8	11.22	49 02	−12.62	36.4	−14 37	21.03
Cl	12.43	49.41	61 84	36.19	98 03	12.87	110 9	10 9	121.8
Br	12.43	64.03	76.46	61 34	137 8	40.7	178.5	35 4	213 91

It will be observed that not only the additive value is different for each successive substitution, it is also not regular. The usual device to satisfy such behaviour is to assume a different additive value for each subsequent substitution, but it is not altogether satisfactory.

It thus appears that the change depends not only on the incoming group but also on the existing groups. Thus, an additivity scheme, based on purely atomic contributions or bonding contributions, does not furnish a satisfactory solution.

Recently Bernstein (*J. Chem. Phys.*, 1951, **19**, 140; 1952, **20**, 263, 524, 1328; 1953, **21**, 2188; *J. Phys. Chem.*, 1952, **56**, 351) has shown that if it be assumed that the contributions due to interactions between non-bonded atoms are also additive, several important properties like heats of formation, bond distances, vibration frequencies, etc. of substituted compounds can be successfully correlated.

It is proposed to show that similar considerations, when applied to T_b^2, lead to fruitful results. Methane and silane derivatives will be considered on a somewhat simplified version of Bernstein's treatment. It may be added that "the physical picture may be one of interaction between charge distributions in bonds and/or interactions between non-bonded atoms and still yield the same algebraic relations between the constitutive properties of molecules".

The absolute values of the contribution due to bonded and non-bonded atoms cannot be evaluated. However, one can be expressed in terms of the other. It is convenient to express the contributions of non-bonded atoms in terms of bonded atoms. For the sake of differentiating, the non-bonded pairs are shown in parenthesis. In calculating the value for a given compound the unknown quantities cancel out.

The contributions due to non-bonded atoms in CH_4 derivatives are shown in Table II. Table III compares the observed and the calculated values. T_b is given in °K and T_b^2 in units of 10^3 (deg.)^2. The following symbols have been used: M—methyl group; E—ethyl group; P—phenyl group. The compounds are arranged in the following order: H, M, E, P, F, Cl, Br, I derivatives. The method of calculations may be illustrated with CH_2Cl_2. There are 2 CH bonds and two C Cl bonds. Further, there is one (HH) non-bonded interaction; one (Cl Cl) non-bonded interaction and four (H Cl) non-bonded interactions. The total value is

$$2\,CH + 2\,C\,Cl = (H\,H) + (Cl\,Cl) + 4\,(H\,Cl)$$
$$= 2\,CH + 2\,C\,Cl + 2.07 - \tfrac{2}{3}\,CH + 20.3 - \tfrac{2}{3}\,C\,Cl + 74.8 - \tfrac{4}{3}\,C\,Cl - \tfrac{4}{3}\,C\,H$$
$$= 97.17$$

which means $T_b^2 = 97.17 \times 10^3$; or $T_b = 311.7$°K. The observed value is 313°K.

The contributions due to non-bonded atoms in SiH_4 derivatives are recorded in Table V. The observed and the calculated values are tabulated in Tables VI to XI. The calculations are similar to that of CH_4 derivatives.

Thus for SiH_2Br_2:

2 SiH + 2 SiBr + (HH) + (Br Br) + 4 (H Br)

= 2 SiH + 2 SiBr + 4.33 $-\frac{2}{3}$ SiH + 30.25 $-\frac{2}{3}$ SiBr + 79.12 $-\frac{4}{3}$ SiBr $-\frac{4}{3}$ SiH

= 113.70

which means $T_b^2 = 113.7 \times 10^3$ or $T_b = 337.2°K$ which compares favourably with the observed value 339°K

The data have been collected from the following sources:

1. Hand Book of Chemistry and Physics, edited by Hodgman, Chemical Rubber Publishing Inc., Ohio.
2. International Critical Tables.
3. Landolt-Börnstein Tabellen.
4. Burkhard-*et al.*, *Chem. Rev.*, 1947, **41**. 97.

Appreciably different values have been found by different workers for the same compound. In such cases usually the more recent value has been utilised.

TABLE II

Carbon compounds.

(Contributions due to non-bonded atoms).

Interaction	Value.	Interaction.	Value.
HH	2.07 $-\frac{3}{8}$ C H	H Cl	18.70 $-\frac{1}{3}$ C Cl $-\frac{1}{3}$ C H
MM	13 30 $-\frac{3}{8}$ C M	H Br	23 60 $-\frac{1}{3}$ C Br $-\frac{1}{3}$ C H
FF	3 51 $-\frac{3}{8}$ C F	MF	13.95 $-\frac{1}{3}$ C F $-\frac{1}{3}$ C M
ClCl	20 30 $-\frac{3}{8}$ C Cl	MCl	20.80 $-\frac{1}{3}$ C Cl $-\frac{1}{3}$ C M
BrBr	35 65 $-\frac{3}{8}$ C Br	MBr	25 94 $-\frac{1}{3}$ C Br $-\frac{1}{3}$ C M.
HM	9 50 $-\frac{1}{3}$ C M. $-\frac{1}{3}$ C H	FCl	9.03 $-\frac{1}{3}$ C Cl $-\frac{1}{3}$ C F.
HF	10.70 $-\frac{1}{3}$ C F $-\frac{1}{3}$ C H.	Cl Br	27 10 $-\frac{1}{3}$ C Cl $-\frac{1}{3}$ C Br

TABLE III

One and two types of linking.

Compound	T_b obs.	T_b calc.	Error. obs.−calc.	Compound.	T_b obs.	T_b calc.	Error. (obs.−calc.).
CH_4	111.5°K	111.5°K	0.0	CMF_3	226.2°K	228.9°K	−2.7
CH_3M	184 6°	186.3°	−1 7	CM_2Cl	324.0°	319 9°	+4.1
CH_2M_2	230 9°	231.1°	−0.2	CM_2Cl_2	342.7°	341.8°	+0.9
CHM_3	262.8°	261.5°	+1.3	$CMCl_3$	347.1°	351.1°	−4.0
CH_3F	194 4°	195.7°	−1.3	CM_2Br	346 3°	343.1°	+3.2
CH_2F_2	221.4°	220.0°	+1 4	CM_2Br_2	387.0°	390.8°	−3.8
CHF_3	190.8°	206.6°	(−15.8)	$CMBr_3$	...	* 429.9°	...
CH_3Cl	248.8°	249 6°	−0 8	CF_4	145.0°	145.0°	0.0
CH_2Cl_2	313.1°	311.7°	+1.4	CF_3Cl	193.0°	194.0°	−1.0
$CHCl_3$	333.0°	342 1°	(−9.1)	CF_2Cl_2	245 0°	244 8°	+0.2
CH_3Br	276.6°	277.5°	−0.9	$CFCl_3$	297.1°	296.7°	+0.4
CH_2Br_2	371.2°	363.4°	+7.8	CCl_4	349 0°	349.0°	0.0
$CHBr_3$	422.5°	421.6°	+0.9	CCl_3Br	377.1°	377.1°	0 0
CM_4	282 5°	282.5°	0.0	CCl_2Br_2	...	* 392.9°	...
CM_3F	...	* 285 9°	...	$CClBr_3$	...	* 433.9°	...
CM_2F_2	272.4°	269.4°	+3.0	CBr_4	462.5°	462.5°	0.0

TABLE IV

Three types of linking.

Compound.	T_b obs.	T_b calc.	Error (obs.−calc)	Compound.	T_b obs.	T_b calc.	Error	Compds	T_b obs.	T_b calc.	Error
MCH_2F	235.3°K	237.6°K	−2.3	M_2CHF	262.9°K	266.3°K	−3.4	$MCHF_2$	248.3°K	249.6°K	−1.3
MCH_2Cl	285.2°	281.5°	+3.7	M_2CHCl	308.0°	304.3°	+3.7	$MCHCl_2$	330.3°	329.8°	+0.5
MCH_2Br	311.0°	306.9°	+4.1	M_2CHBr	332.6°	328.3°	+4.3	$MCHBr_2$	381.0°	379.8°	+1.2

TABLE V

Silicon compounds.

(Contributions due to non-bonded atoms).

Interaction.	Value.	Interaction.	Value.	Interaction.	Value.
HH	4.33−⅔ SiH	HF	7.12−½ SiF −½ SiH	EP	55.14−½ SiP−½SiE
MM	14.95−⅔ SiM	HCl	14.13−½ SiCl −½ SiH	EF	18.75−½ SiE−½ SiF
EE	30.25−⅔ SiE	HBr	19.78−½ SiBr−½ SiH	ECl	27.77−½ SiE−½ SiCl
PP	81.90−⅔ SiP	HI	28.17−½ SiI −½ SiH	EBr	8.05−½ SiBr−½ SiE
FF	5.28−⅔ SiF	ME	22.74−½ SiM −½ SiE	PF	43.70−½ SiP−½ SiF
ClCl	18.21−⅔ SiCl	MP	50.92−½ SiM −½ SiP	PCl	58.16−½ SiP−½ SiCl
BrBr	30.25−⅔ SiBr	MF	13.71−½ SiM −½ SiF	PBr	23.26−½ SiP−½ SiBr
II	52.83−⅔ SiI	MCl	20.85−½ SiM −½ SiCl	FCl	10.25−½ SiCl−½ SiF
HM	11.32−½ SiM−½ SiH	MBr	25.65−½ SiM −½ SiBr	ClBr	23.40−½ SiBr−½SiCl
HE	17.88−½ SiE−½ SiH			ClI	31.46−½ SiI−½ SiCl

TABLE VI

SiH_4 *and its derivatives.*

Compound.	T_b obs.	T_b calc.	Error.	Compound.	T_b obs.	T_b calc.	Error.	Compound	T_b obs.	T_b calc.	Error.
SiH_4	161.2°K	161.2°K	0.0	SiH_3F	—	*185.0°	0.0	SiH_3Br	274.9°K	269.0°K	+5.9
SiH_3M	216.7°	216.7°	0.0	SiH_2F_2	—	*195.1°		SiH_2Br_2	339.0°	337.2°	+1.8
SiH_2M_2	254.1°	254.1°	0.0	$SiHF_3$	192.8°	192.8°	0.0	$SiHBr_3$	382.0°	387.4°	−5.4
$SiHM_3$	280.7°	280.7°	0.0	SiH_3Cl	242.6°	235.4°	+7.2	SiH_3I	—	*312.2°	
SiH_3E	258.2°	258.2°	0.0	SiH_2Cl_2	281.3°	281.2°	+0.1	SiH_2I_2	—	*412.1°	
SiH_2E_2	325.8°	325.8°	0.0	$SiHCl_3$	306.0°	311.4°	−5.4	$SiHI_3$	493.0°	493.0°	0.0
$SiHE_3$	380.0°	380.0°	0.0								

TABLE VII

SiM_4 *and its derivatives.*

Compound.	T_b obs.	T_b calc.	Error.	Componnd.	T_b obs.	T_b calc.	Error
SiM_4	299.5°K	299.5°K	0.0	SiM_2F_2	275.7°K	275.0°K	+0.7
SiM_3E	335.0°	336.2°	−1.2	$SiMF_3$	242.8°	238.6°	+4.2
SiM_2E_2	368.8°	369.0°	−0.2	SiM_3Cl	330.3°	327.7°	+2.6
$SiMF_3$	400.0°	398.7°	+1.3	SiM_2Cl_2	343.0°	341.3°	+1.7
SiM_3P	444.6°	444.6°	0.0	$SiMCl_3$	339.0°	342.4°	−3.4
SiM_2P_2	—	*548.1°		SiM_3Br	353.0°	349.0°	+4.0
$SiMP_3$	—	*631.3°		SiM_2Br_2	385.3°	384.5°	+0.8
SiM_3F	289.4°	293.2°	−3.8	$SiMBr_3$	406.5°	409.6°	−3.1

TABLE VIII

SiE_4 *and derivatives.*

Compound.	T_b obs.	T_b calc.	Error.	Compound	T_b obs.	T_b calc.	Error.
SiE_4	426.0°K	426.0°K	0.0	SiE_3Cl	416.5°K	417.1°K	−0.6
SiE_3P	512.0°	506.2°	+5.8	SiE_2Cl_2	402.0°	399.3°	+2.7
SiE_2P_2	570.0°	576.8°	−6.8	$SiECl_3$	379.9°	371.3°	−0.4
$SiEP_3$	—	* 641.2°		SiE_3Br	339.5°	339.5°	0.0
SiE_3F	382.0°	383.4°	−1.4	SiE_2Br_2	..	* 304.5°	
SiE_2F_2	333.9°	332.4°	+1.5	$SiEBr_3$	...	* 339.5°	
$SiEF_3$	269.0°	268.5°	+0.5				

TABLE IX

SiP_4 *and derivatives.*

Compounds.	T_b obs.	T_b calc.	Error.	Compounds.	T_b obs.	T_b calc.	Error.
SiP_4	701.0°K	701.0°K	0.0	SiP_2Cl_2	578.2°K	576.8°K	+1.4
SiP_3F	478.0°	376.8°	(101.2)	$SiPCl_3$	474.5°	478.6°	−4.1
SiP_2F_2	520.0°	511.8°	(+8.2)	SiP_3Br	...	*561.6°	
$SiPF_3$	375.0°	383.3°	(−8.3)	SiP_2Br_2	453.0°	453.0°	
SiP_3Cl	651.0°	648.3°	+2.7	$SiPBr_3$	...	*400.6°	0.0

TABLE X

Si (Hal)$_4$ *and derivatives.*

Compounds.	T_b obs.	T_b calc.	Error.	Compounds	T_b obs.	T_b calc.	Error.
SiF_4	178.0°K	178.0°K	0.0	$SiCl_3Br$	353.0°K	353.2°K	−0.2
SiF_3Cl	216.0°	215.8°	+0.2	$SiCl_2Br_2$	377.0°	376.9°	+0.1
SiF_2Cl_2	254.0°	254.0°	0.0	$SiClBr_3$	413.5°	401.1°	(+12.4)
$SiFCl_3$	292.0°	292.2°	−0.2	$SiBr_4$	426.0°	426.0°	0.0
$SiCl_4$	330.5°	330.5°	0.0	SiI_4	563.0°	563.0°	0.0

TABLE XI

Three types of linking.

Compounds.	T_b obs.	T_b calc.	Error.	Compounds.	T_b obs.	T_b calc.	Error.
$MSiF_3Cl$	272.5°K	272.1°K	+0.4	$ESiP_2Cl$	300.2°K	301.7°K	−1.5
$MSiFCl_2$	302.5°	306.8°	−4.3	$ESiPCl_2$	335.2°	336.2°	−1.0
$MSiHCl_2$	314.0°	315.4°	−1.4	$ESiPCl_3$	503.0°	495.2°	+7.8
$MSiH_2Cl$	281.0°	275.8°	+5.2	M_2SiFCl	309.4°	307.2°	+2.2

It will be observed that the agreement between the observed and calculated values is satisfactory, the mean error for methane derivatives being ($\pm$1.87) and ($\pm$1.72) for

* Values marked with asterisk are the predicted ones on the basis of the proposed scheme.

silane derivatives. (Errors shown in parenthesis have not been taken for computing mean errors). However, for a few compounds there are large errors. It is quite probable that the experimental values may be in error for these. As mentioned earlier, often values reported by two workers differ considerably. In some cases a slightly higher power, viz. $T_b^{\frac{2}{3}}$ seems to give somewhat better results; however, the data are not accurate enough to warrant the detailed calculations.

The authors have much pleasure in thanking Dr. K. Majumdar for his interest in this investigation.

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GLYCOLATE COMPLEX OF TRIVALENT ANTIMONY

By G. Patra and S. Pani

When antimonous oxide is treated with partially neutralised glycolic acid, the complex (I) is formed in the solution. The concentration of the complex in the solution first increases to a maximum value and then decreases with increasing p_H. The equilibrium constant of the reaction at 35° is 7.38×10^6.

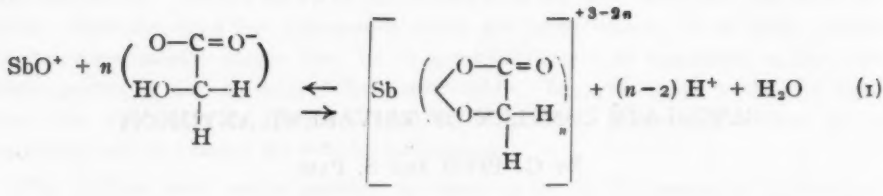
No quantitative work appears to have been done on glycolate complex of antimony. As a chelate glycolate ion practically does not differ from lactate ion, it is expected that the same type of complex of antimony would be produced by glycolate ion, as reported by Mohanty and Pani (this *Journal*, 1954, **31**, 593). The results confirm the above assumption. The equilibrium constant of the reaction has also been determined.

Experimental

The chemicals used were of Analar quality. The solubility of antimony oxide at 35° in partially neutralised solutions of glycolic acid of known concentrations, and p_H of the solutions at equilibrium were determined as done by Mohanty and Pani (*ioc. cit.*). The results are shown in Table I.

Extent of neutralisation of glycolic acid.	Total glycolate (g. mol./litre of solr.).	p_H.	Total Sb per litre.	Total complex per litre. $[Sb] \times 10^3$.	Total glycolate ion per litre. $[GOH^-] \times 10^2$.	$K \times 10^{-6}$.
	0.30	3.52	13.96×10^{-3}	13.90	10.68	5.24
25%	0.20	3.25	7.37	7.312	4.771	7.41
	0.10	3.26	2.22	2.162	2.503	8.16
	0.08	3.28	1.53	1.472	2.084	8.38
	0.06	3.31	0.94	0.882	1.655	8.54
	0.05	3.34	0.71	0.652	1.453	8.78
50	0.40	3.82	26.30	26.24	19.55	5.89
	0.35	3.77	23.30	23.24	16.22	6.76
	0.30	3.78	18.95	18.89	14.16	7.37
	0.25	3.77	14.00	13.94	11.86	7.58
	0.20	3.78	9.85	9.792	9.74	8.08
	0.10	3.75	2.95	2.892	4.92	8.72
75	0.40	4.39	20.55	20.49	29.69	7.41
	0.35	4.34	12.10	12.04	26.40	4.91
	0.30	4.35	10.55	10.49	22.69	5.93
	0.25	4.34	7.75	7.692	19.00	6.06
	0.20	4.34	6.45	6.302	15.16	7.90
	0.10	4.30	2.225	2.167	7.60	9.72
						Mean 7.38

It is assumed that n glycolate ions react with an antimonyl ion (SbO^+). The reaction is shown by equation (1) and the equilibrium constant by the reaction (2) where [Sb], $[H^+]$, $[SbO^+]$ and $[GOH^-]$ represent the molar concentrations of the complex, H^+ ion, antimonyl ion and glycolate ion respectively.



$$\frac{[Sb] \times [H^+]^{(n-2)}}{[SbO^+] \times [GOH^-]^n} = K \qquad \ldots \qquad \ldots \qquad \ldots \quad (2)$$

Substituting $[SbO^+]$ by $7.7 \times 10^{-4} \times [H^+]$ (Gayer and Garrett, *J. Amer. Chem. Soc.*, 1952, **74**, 2353) we get

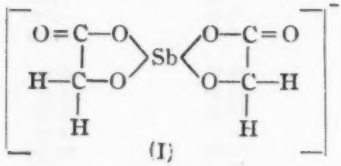
$$\frac{[Sb] \times [H^+]^{(n-3)}}{7.7 \times 10^{-4} \times [GOH^-]^n} = K \qquad \ldots \qquad \ldots \quad (3)$$

The concentration of H^+ being very nearly constant, for each set of experiments (glycolic acid has been neutralised to the same extent),

$$\frac{[Sb]}{[GOH^-]^n} = K_1 \qquad \ldots \qquad \ldots \qquad \ldots \quad (4)$$

and $$\log [Sb] = \log K_1 + n \log [GOH^-] \qquad \ldots \qquad \ldots \quad (5)$$

By plotting log [Sb] against log $[GOH^-]$ straight lines would be obtained and the slope would give the value of n. [Sb] was obtained by subtracting the solubility of antimony oxide (5.8×10^{-5} g. atom of Sb/1000 g. of water at 30° ; Gayer *et al.*, *loc. cit.*) from total antimony in the solution. $[GOH^-]$ was calculated as for lactate ion (Mohanty and Pani, *loc. cit.*) from p_H of the solution, dissociation constant of glycolic acid (1.95×10^{-4}; Cannan and Kribrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314) and the unreacted glycolate in the solution. n is found to be very nearly 2 in all the three sets of experiments. The complex is most probably



(I)

The reaction may be represented by equation (6) and the equilibrium constant, by equation (7).

$$SbO^+ + 2\ CH_2(OH).COO^- \rightleftharpoons (I) + H_2O \qquad \ldots \quad (6)$$

$$\frac{[Sb]}{7.7 \times 10^{-4} \times [H^+] \times [GOH^-]^2} = K \qquad \ldots \quad (7)$$

The values of K calculated are shown in the table, the mean value being 7.38×10^6.

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HEAT OF NEUTRALISATION OF ALKALIES BY CHARCOAL

By Balwant Rai Puri, P. C. Gupta and M. L. Lakhanpal

Heats of neutralisation of hydroxides of Na, K, NH_4 and Ba by five different samples of charcoal were determined. The values were found to be nearly the same for every sample and to be in good agreement with the known heats of neutralisation of these alkalies by carbonic acid.

It is well known that surface oxygen complexes are formed on all types of carbon and that they are removed only at high temperatures as oxides of carbon (Lowry and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 1408; Rideal and Wright, *J. Chem. Soc.*, 1925, 1347; Shah, *ibid.*, 1929, 2661; Anderson and Emmett, *J. Phys. Chem.*, 1947, **51**, 1308; 1952, **56**, 753). It is also known that these complexes increase the capacity of charcoal to adsorb alkalies and decrease its capacity to adsorb acids (King, *J. Chem. Soc.*, 1937, 1489; Weller and Young, *J. Amer. Chem. Soc.*, 1948, **70**, 4155). No satisfactory explanation for these properties appears to have been suggested.

Puri *et al.* (*Soil Sci.*, 1953, **75**, 209) regard "base adsorption" by charcoal as a neutralising reaction on account of the presence of CO_2 as a surface compound in the complex. According to them, charcoal, when suspended in water, ionises as

$$\mathbf{O}\text{-}CO_2 + H_2O \rightarrow \mathbf{O}\text{-}CO_3^{2-} \mid 2H^+,$$

where the circle represents the charcoal surface and -C represents a surface carbon atom. The hydrogen ions being directed towards the liquid react with alkalies as

$$\mathbf{O}\text{-}CO_3^{2-} \mid 2H^+ + 2NaOH \rightarrow \mathbf{O}\text{-}CO_3^{2-} \mid 2Na^+ + 2H_2O$$

resulting in the exchange of H^+ ions by the alkali cations and the formation of water. The authors adduced evidence in favour of this view by showing that the various samples of charcoal examined by them could remove different alkalies as well as bring about decomposition of carbonates and sulphides in stoichiometric relations.

If this view is correct then the heat evolved during neutralisation of an alkali by different samples of charcoal should necessarily be the same and almost identical with the value obtained when the same alkali is neutralised by carbon dioxide.

Experimental

Five samples of charcoal obtained by the carbonisation of cane sugar, cocoanut shell, pine wood, acacia wood and cotton-stalks were used in these investigations. They were rendered 'ash-free' by HF-HCl treatment and then exposed to an atmosphere of oxygen for about 24 hours at the room temperature.

Neutralisation of Alkalies.—Each sample (0.5 g.) was mixed with 80 ml. of 0.4 *N* solutions of $Ba(OH)_2$, NaOH, KOH and NH_4OH and the suspensions shaken mechanically for about 48 hours. The amount of the unused alkali was determined by titrating an aliquot of the clear supernatant liquid against a standard acid solution.

This method has been shown (Puri *et al., loc. cit.*) to afford the maximum capacity of charcoal to neutralise alkali which does not increase further on increasing the time of the reaction or the concentration of the alkali solution. The slowness of the reaction obviously is due to the slow rate of diffusion of the alkali through the narrow pores of charcoal.

Heat of Neutralisation of Alkalies.—The thermal effect produced during the neutralisation of different alkalies by the various samples of charcoal was determined calorimetrically by the technique described by Gregg ("The Surface Chemistry of Solids", 1951, p. 241, Chapman & Hall). A Beckmann thermometer was used to measure the rise of temperature.

About 5 g. of charcoal was suspended in 25 ml. of CO_2-free distilled water in a glass bulb and the suspension shaken for a few minutes in order to attain proper wetting. The bulb was immersed in 200 ml. of 0.4 *N* alkali solution contained in the calorimeter for more than an hour. The solution was stirred gently. When the temperature became steady, the bulb was broken. The rise of temperature was recorded after every 5 minutes. The rate of rise of temperature decreased after about an hour and a half. The stirring was then discontinued and 20 ml. of the clear supernatant liquid was withdrawn soon afterwards and the amount of the unchanged alkali determined in the usual manner.

The amount of alkali, neutralised by charcoal during this interval, usually varied from 30 to 40% of the maximum capacity of charcoal to neutralise alkalies. The heat evolved during the reaction was obtained from the knowledge of the thermal capacity of the system and the rise in its temperature. From the known amount of alkali neutralised, the heat evolved for the neutralisation of 1 g. equivalent of alkali could be easily calculated. The amounts of different alkalies neutralised by the various samples of charcoal are recorded in Table I.

TABLE I

Amount of different alkalies neutralised by various samples of charcoal.

Alkali.	Amount (m.e./100 g.) neutralised by the samples of charcoal from				
	Sugar.	Cocoanut shell.	Pine wood.	Acacia wood.	Cotton-stalk.
$Ba(OH)_2$	968.0	715 5	545 7	476.6	495 0
NaOH	998.3	710.5	561.8	460.1	509.2
KOH	989.5	735.2	543 1	461.3	514.6
NH_4OH	517.5	406.6	338.1	316.7	262.4

DISCUSSION.

It is interesting to note that sodium hydroxide, potassium hydroxide and barium hydroxide solutions are neutralised in equivalent proportions. Ammonium hydroxide, however, is neutralised to a smaller extent. This may be due to its being a weak base and consequently its inability to neutralise completely a weak acid like CO_2. There is also a possibility of larger steric hindrance to the diffusion of NH_4^+ ion into smaller

pores on account of its comparatively large ionic radius (1.48 Å) with respect to those of Na^+ (0.95 Å), K^+(1.33 Å) and Ba^{2+} (1.35 Å). These observations are consistent with the results obtained earlier (Puri *et al.*, *loc. cit.*). It may be mentioned incidentally that even with sodium hydroxide and potassium hydroxide, the formation of carbonate ion in solution is very small. This is obviously due to the carbonate ions being fixed on the charcoal surface in accordance with the equation shown above.

The heats of neutralisation of the various alkalies by different samples of charcoal are recorded in Table II. It is interesting to note that the heat of neutralisation of a given alkali is nearly the same for every sample of charcoal, irrespective of its nature and capacity to neutralise alkalies. The reaction involved therefore appears to be identical in every case.

TABLE II

Heats of neutralisation of different alkalies by various samples of charcoal and carbonic acid.

Alkali.	Sugar charcoal.	Cocoanut shell charcoal.	Pine wood charcoal.	Acacia wood charcoal.	Cotton stalk charcoal.	Carbonic acid.
	Heat evolved in k. cals /g. equiv.					
$Ba(OH)_2$	11.23	11.31	11.18	11.40	10.88	11.06
NaOH	10.30	10.01	10.38	10.89	10 41	10.10
KOH	10.14	10 43	10.34	10.40	10.06	10 10
NH_4OH	8.61	8.35	8.57	8.49	8 54	8 10

The heats of neutralisation of the various alkalies by carbonic acid, taken from standard literature, are also included in Table II for the sake of comparison. The values are in good agreement with those obtained in the case of the various samples of charcoal. These results therefore support the suggestion that the removal of alkalies by charcoal is due to their neutralisation by CO_2 of the oxygen complex as represented by the equation shown above.

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COMPLEX COMPOUNDS OF NICKEL AND COPPER WITH *p*-TOLYLBIGUANIDE

By S. P. Ghosh and A. K. Chatterjee

Several complex compounds of nickel and copper with *p*-tolylbiguanide have been prepared and their properties described. Because of the favourable 'size factor' of the co-ordinating molecule the nickel complexes exhibit different colour modifications The nickel-*p*-tolylbiguanidinium hydroxide has been obtained in three different modifications of which the α-variety, with light orange colour, is the most stable. In case of the copper complexes, however, only one variety of compounds could be prepared.

We have previously reported (this *Journal*, 1953, **30**, 369) the complex compounds of nickel and copper with phenylmethylbiguanide. No evidence could be obtained on the *cis-trans* isomerism of four-covalent nickel and copper complexes with this co-ordinating molecule, though the so-called 'size factor' was more favourable than phenylbiguanide with which Rây and Chakravarty (*ibid.*, 1941, **18**, 609) reported evidences regarding such isomerism. In the present communication the results of our investigation on such isomerism with *p*-tolylbiguanide is recorded. This co-ordinating molecule has the same molecular weight as that of the phenylmethylbiguanide, but there is a difference in the position of the methyl group. The 'size factor' might therefore show a different influence. This is actually so, as it has been possible to isolate the nickel-*p*-tolylbiguanidinium hydroxide in three different modifications. The halides and the sulphate of the complex nickel base were also obtained in different modifications. In the case of copper complexes, only one type of compounds could be prepared. α-Nickel-*p*-tolylbiguanidinium hydroxide was found to be the most stable with light orange colour. The pink coloured β-hydroxide changed to the light orange α-variety on warming with water. The yellow γ-hydroxide also changed to the light orange α- variety in presence of a drop of dilute acetic acid. From the colour of the complex salts these complexes are assumed to be of the planar type with dsp^2 hybrid bonds.

Experimental

p-Tolylbiguanide hydrochloride ($C_9H_{13}N_5$. HCl) was prepared by refluxing for about 2 hours an equimolecular mixture of dicyandiamide and *p*-toluidine hydrochloride in alcohol. The mixture on cooling deposited white crystals of the hydrochloride. These were purified by recrystallisation from water.

Nickel Compounds

α-*Nickel-p-tolylbiguanidinium Hydroxide*.—Freshly prepared sodium hydroxide solution was added dropwise to a solution of nickel sulphate (1 mole) and *p*-tolylbiguanide hydrochloride (2 moles), when a light pink precipitate of the complex base separated. The colour gradually changed to light orange. The precipitate was rapidly

filtered, washed with cold water and then with cold alcohol. The substance was dried over sodium hydroxide. {Found: Ni, 12.38; N, 29.48. [Ni (*p*-tolyl-BigH$^+$)$_2$] (OH)$_2$ requires Ni, 12.36; N, 29.49 per cent} (where *p*-tolyl-BigH$^+$ = one molecule of *p*-tolylbiguanide = $C_9H_{13}N_5$).

β-Nickel-p-tolylbiguanidinium hydroxide was obtained by the addition of dilute ammonium hydroxide to a solution of nickel sulphate (1 mole) and *p*-tolylbiguanide hydrochloride (2 moles). Excess of ammonia was avoided. A pink coloured precipitate was at once obtained. This was filtered, washed and dried as in the previous case. {Found : Ni, 12.41; N, 29.51. [Ni(*p*-tolyl-BigH$^+$)$_2$] (OH)$_2$ requires Ni, 12.36; N, 29.49 per cent}.

γ-Nickel-p-tolylbiguanidinium Hydroxide.—When a small quantity of dilute ammonia was added to a hot solution of nickel sulphate and *p*-tolylbiguanide hydrochloride, a light pink precipitate was obtained. On treatment of this precipitate with further quantity of ammonium hydroxide on the water-bath, the pink base at once changed to yellow. The yellow precipitate was filtered, washed and dried as above. {Found: Ni, 12.43; N, 29.55. [Ni(*p*-tolyl-BigH$^+$)$_2$] (OH)$_2$ requires Ni, 12.36; N, 29.49 per cent}.

α-Nickel-p-tolylbiguanidinium Chloride.—The complex base was suspended in water and was treated with an excess of ammonium chloride on the water-bath till the evolution of ammonia had ceased. The yellowish buff-coloured precipitate was thoroughly washed with water by decantation, filtered, washed with alcohol and dried in air. {Found: Ni, 10.19; Cl, 12.52; N, 24.70. [Ni (*p*-tolyl-BigH$^+$)$_2$] Cl$_2$ 3H$_2$O requires Ni, 10.37; Cl, 12.52; N, 24.75 per cent}.

The *β*-base on similar treatment, however, produced the same yellowish buff-coloured precipitate as the α-chloride.

An orange-yellow chloride was, however, obtained on treating the yellow γ-base with ammonium chloride. The precipitate was filtered, washed and dried as above. {Found: Ni, 10.37; Cl, 12.48. [Ni(*p*-tolyl-BigH$^+$)$_2$ Cl$_2$. 3H$_2$O requires Ni, 10.37; Cl, 12.53 per cent}.

α-Nickel-p-tolylbiguanidinium Bromide.—Like the chloride this was obtained by the action of ammonium bromide on the α-base and heating on the water-bath till the evolution of ammonia had ceased. The light buff-coloured precipitate was filtered, washed with water and alcohol and then dried in air. {Found: Ni, 9.54; Br, 26.05. [Ni (*p*-tolyl-BigH$^+$)$_2$ Br$_2$.H$_2$O requires Ni, 9.49; Br, 25.84 per cent}.

When the *β*-base was treated as above, a light buff-coloured precipitate, similar to the α-bromide, was obtained.

From the γ-base, by the action of ammonium bromide, a deep buff-coloured bromide was obtained. This was filtered, washed and dried as usual. {Found: Ni, 9.53; Br, 25.98. [Ni(*p*-tolyl-BigH$^+$)$_2$] Br$_2$. H$_2$O requires Ni, 9.49; Br, 25.84 per cent}.

α-Nickel-p-tolylbiguanidinium iodide was prepared by the action of ammonium iodide on the complex base. When the evolution of ammonia had ceased, the buff coloured precipitate was filtered, washed with water and alcohol and dried in air. The substance was slightly soluble in alcohol. {Found : Ni, 8.45; I, 36.37. [Ni(*p*-tolyl-BigH$^+$)$_2$]X$_2$ requires Ni, 8.47; I, 36.54 per cent}.

α-Nickel-p-tolylbiguanidinium Sulphate.—A buff coloured substance was obtained by the action of ammonium sulphate on the base. The substance was kept on the water-bath till the evolution of ammonia had stopped. It was then filtered, washed with water and alcohol, and dried in air. It was found to be less soluble than than the α-chloride. {Found : Ni, 9.89; SO_4, 16.18. $[Ni(p\text{-tolyl-BigH}^+)_2]SO_4.3H_2O$ requires Ni 9.93 ; SO_4, 16.25 per cent}.

The sulphate prepared from the β-base was similar to the α-sulphate.

The γ-sulphate was obtained in a similar way from the γ-base. It was orange-yellow in colour. (Found : Ni, 9.90%; SO_4, 16.21%).

α-Nickel-p-tolylbiguanidinium nitrate was obtained as a light buff-coloured substance by the action of ammonium nitrate on the α-base. The substance was found to be moderately soluble in water. It was filtered, washed with ice-cold water and alcohol, and dried in air. {Found : Ni, 10.18 ; N, 28.63. $[Ni(p\text{-tolyl-BigH}^+)_2](NO_3)_2.H_2O$ requires Ni, 10.07 ; N, 28.83 per cent}.

Copper Compounds

Copper-p-tolylbiguanidinium Hydroxide.—When an ammoniacal copper sulphate solution was added slowly to that of *p*-tolylbiguanide hydrochloride in water, a dirty violet precipitate was obtained. This was purified by dissolving the precipitate in the minimum quantity of dilute hydrochloric acid and then precipitating the base with dilute and freshly prepared sodium hydroxide solution. The precipitate was rapidly filtered, washed with cold water and alcohol, and dried to a constant weight over sodium hydroxide. It evolved ammonia from ammonium salts. {Found : Cu, 13.23 ; N, 29.29. $[Cu(p\text{-tolyl-BigH}^+)_2](OH)_2$ requires Cu, 13.25; N, 29.19 per cent}.

The *chloride* was obtained by the action of ammonium chloride on an aqueous suspension of the base on the water-bath. When the evolution of ammonia had ceased, the bluish pink precipitate was filtered, washed with water and alcohol and dried in air. {Found : Cu, 10.57 ; Cl, 11.72. $[Cu(p\text{-tolyl-BigH}^+)_2]Cl_2.5H_2O$ requires Cu, 10.47; Cl, 11.69 per cent}.

The *bromide* was similarly obtained, as a pink coloured substance, by the action of ammonium bromide on the complex base. {Found : Cu, 10.53; Br, 26.57. $[Cu(p\text{-tolyl-BigH}^+)_2]Br_2$ requires Cu, 10.50 ; Br, 26.40 per cent}.

The *iodide* was obtained by the action of ammonium iodide on the base. It was dull pink in colour, sparingly soluble in water but moderately so in alcohol. {Found : Cu, 9.12 ; I, 36.38. $[Cu(p\text{-tolyl-BigH}^+)_2]I_2$ requires Cu, 9.08 ; I, 36.29 per cent}.

The *sulphate* was a violet crystalline substance and was obtained by the action of ammonium sulphate on the complex base in the usual way. {Found : Cu, 11.72 ; SO_4, 17.69. $[Cu(p\text{-tolyl-BigH}^+)_2]SO_4$ requires Cu, 11.73 ; SO_4, 17.72 per cent}.

The *nitrate* was obtained by the action of ammonium nitrate on the complex base. It was filtered, washed and dried in the usual way. It was pink in colour and was found to be more soluble in water than the chloride. {Fouud : Cu, 10.82; N, 28.52. $[Cu(p\text{-tolyl-BigH}^+)](NO_3)_2.H_2O$ requires Cu, 10.81 ; N, 28.59 per cent}.

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DISCONTINUITIES IN THE ADSORPTION OF POLYBASIC ACIDS, HYDROXYBENZENES AND BI-SALTS FROM AQUEOUS SOLUTION ON SILICA GEL

By K. D. Jain

The adsorption of mono-, di- and tricarboxy acids, organic and inorganic, bi-salts of dibasic acids, and mono- and dihydroxybenzenes from aqueous solutions by activated silica gel has been studied. Adsorption of monocarboxy acids on silica gel approximately follows the equation $x/m = KC^{\frac{1}{n}}$ and may therefore be mainly a simple adsorption phenomenon. Adsorption of polybasic acids, both organic and in organic, bi-salts and hydroxybenzenes gives a discontinuous isotherm.

New and conclusive evidence for the existence of discontinuous adsorption has been obtained with aqueous solutions of different organic aliphatic and aromatic polybasic acids, bi-salts of dibasic acids and hydroxybenzenes on activated sugar charcoal by Jain and Jha (this *Journal*, 1940, **17**, 685; 1941, **18**, 321, 585). To study the behaviour of these adsorbates on other adsorbents, experiments were conducted on silica gel under similar conditions, and the adsorption of monobasic acids was found continuous, while that of polybasic acids, bi-salts of dibasic acids, phenol and hydroquinone, discontinuous and irregular with maxima and minima at different equilibirium concentrations.

Adsorption of monobasic acids in organic solvents by silica gel was studied by Patrick and Jones (*J. Phys. Chem.*, 1925, **29**, 1), Holmes and McKelvey (*ibid.*, 1928, **32**, 1522), Elder and Springer (*ibid.*, 1940, **44**, 943) and Dhar (*Z. anorg. Chem.*, 1926, **155**, 298). and they obtained continuous curves.

Experimental

Preparation of Silica gel.—A solution of sodium silicate was treated with dilute hydrochloric acid, and then ammonium hydroxide was added. The mixture was allowed to set to a jelly from which sodium chloride, hydrochloric acid and ammonium chloride were removed completely by washing with hot distilled water. The purification from the above impurities in the gel took 15 days' working, about 10 hours daily. The product so obtained was tasteless and free from electrolytes. The grains were clear and colorless. It was then dried, ground to a fine powder, passed through a 60-mesh sieve, activated at 250°-260° for about 4 hours and then kept in well stoppered bottles. The activated gel had a water content of 3.32% as determined by ignition to a constant weight in a silica crucible at blast lamp heat.

Analysis.—The adsorption experiments were carried out by weighing exactly 0.5 g. of the gel in clear, dry, glass bottles, similiar in size, to which 100 c.c. portions of the acid solution of varying concentrations in freshly prepared distilled water were pipetted. The bottles were stoppered and shaken for the same length of time (30 minutes) and kept for about 20 hours at the room temperature, usually around 19°, at the end of which interval the equilibrium concentration of the solute (C_e) was determined in the supernatant liquid

by the usual analytical methods. At the same time a blank without the gel was run under the same conditions and the concentration (C_o) was determined. The amount of adsorption (x) was determined by difference and x/m, the amount of adsorption per g. of silica gel, was then calculated. The experiments were repeated with every care.

Estimation of phenol and quinol was carried out as in a previous paper (Jain and Jha, *loc. cit.*, 1941). Some of the results are shown in Fig. 1.

The following table gives an idea about the shape of the discontinuous curves shown in the figures.

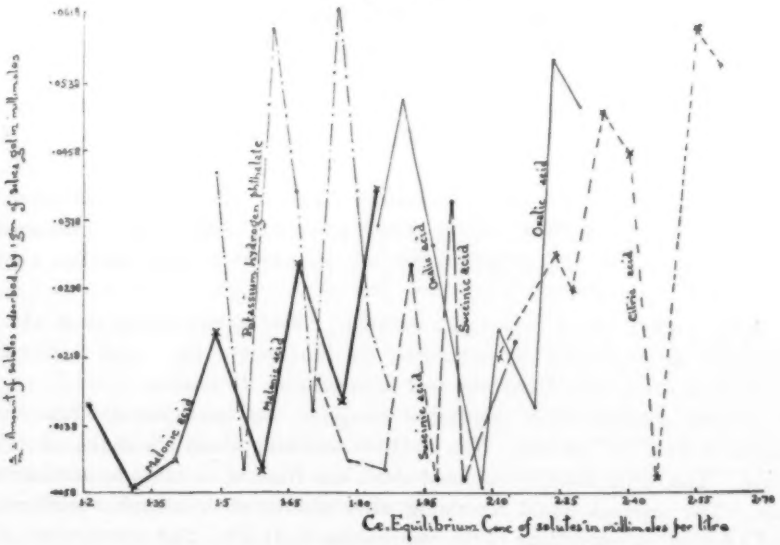
TABLE I

Molar conc. at the max. & min. pts. on the curves.	Diff. in molar conc. between two max & min pts.	Molar conc. at the max. & min. pts. on the curves	Diff. in molar conc. between two max & min pts.
Oxalic acid.		Citric acid.	
0.0178	...	0.01242	—
0.0174	0.0004	0.01190	0.00052
0.0168	0.0006	0.01143	0.00047
0.0166	0.0002	0.01127	0.00026
0.0151	0.0015	0.01085	0.00032
		0.01059	0.00026
Succinic acid.		Phthalic acid.	
0.01715	...	0.00211	...
0.01673	0.00042	0.00190	0.00021
0.01627	0.00046	0.00185	0.00005
0.01584	0.00043	0.00175	0.00010
0.01452	0.00132	0.00162	0.00013
Malonic acid.		Sulphuric acid.	
0.0184	...	0.0126	...
0.0170	0.0014	0.0123	0.0003
0.0160	0.0010	0.0116	0.0007
0.0153	0.0007	0.0110	0.0006
0.0143	0.0010	0.0095	0.0015
0.0126	0.0017	0.0092	0.0003
0.0116	0.0010	0.0080	0.0012
		0.0074	0.0006
Phosphoric acid.		Potassium hydrogen phthalate.	
0.00607	...	0.0092	...
0.00555	0.00052	0.0086	0.0006
0.00504	0.00051	0.0084	0.0002
0.00480	0.00024	0.0076	0.0008
0.00454	0.00026	0.0073	0.0003
0.00432	0.00023		
0.00380	0.00052		
0.00354	0.00026		
Phenol.		Hydroquinone.	
0.0030	...	0.00113	...
0.0027	0.0003	0.00111	0.00002
0.0025	0.0002	0.00105	0.00006
0.0024	0.0001	0.00093	0.00012
0.0023	0.0001	0.00084	0.00009

DISCUSSION

In the previous work (*loc. cit.*) the adsorption on sugar charcoal was found to be greatly influenced by the basicity of the acids. The adsorption on silica gel from aqueous solutions now confirms previous observations. It is found that the adsorption isotherm in the case of monobasic acids is invariably a straight line, while in the case of polybasic acids, organic and inorganic, bi-salt of phthalic acid, and mono- and dihydroxybenzenes, zigzag curves are obtained which appear to be periodic. Some of the results are shown in Fig. 1.

FIG. 1



In each case (Table I) the difference between the equilibrium molar concentrations at the maxima and minima points is multiple, although in some cases it is not so. This may be due to their displacement from their right places. If the points were taken more closely, a definite periodic curve might be obtained.

In explaining the behaviour of these substances on the surface of sugar charcoal, electrometric study of the rate of adsorption of acids by sugar charcoal (Jain, this *Journal*, 1953, **30**, 772) may be suggested for the complexity occurring on the surface of the adsorbent. Further work is being done and it is hoped that some explanation might be forthcoming.

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ESSENTIAL OIL FROM *BRUNELLA VULGARIS*, LINN.

By K. K. Baslas

The essential oil of *Brunella vulgaris*, Linn has been found to consist mainly of *d*-camphor and *d*-fenchone and traces of fenchyl alcohol.

The plant of *Brunella vulgaris*, Linn., popularly known in vernacular as Ustakhadus, is indigenous to India and belongs to N.O. Labiatae. It occurs on Himalayas and on the hills of South India (Nilgiris and Travancore). It is considered to have expectorant and antispasmodic properties. The leaves are used in piles as an external application and the plant as a whole is used for fevers and coughs and is considered antirheumatic and alternative tonic (Kartikar and Basu, "Indian Medicinal Plants", Vol. III, p. 2007).

On steam distillation, a brownish coloured essential oil was obtained (from dried whole overground plant and flowering tops) in 0.4 to 0.6% yield. The oil possesses the following properties: d^{26}, 0.9531; n_D^{30}, 1.4681; ; $[\alpha]_D^{30}$, +35°30, acid number, 1.4—1.8; ester value, 13.1.

On being cooled, the oil deposited a granular, colorless, crystalline mass which had been identified as *d*-camphor by preparing its functional derivatives and comparing their melting points with those prepared from genuine *d*-camphor.

The filtrate obtained after removal of camphor was fractionated when majority of it distilled at 68.5°-69°/10 mm. The residue comprising about 1% of the oil solidified on cooling. The main fraction obtained above was freed of camphor by semicarbazone formation. The residual liquid remaining after removal of the camphor semicarbazone furnished a ketone corresponding to the composition $C_{10}H_{16}O$. The component present in this fraction does not reduce Fehling's solution or ammoniacal silver nitrate solution and also does not form any solid derivative, characteristic of hyrdoxyl group.

From the boiling point and the results of the analysis of the ketone and from the melting point of its oxime, semicarbazone and 2 : 4-dinitrophenylhydrazone, the ketone has been identified as *d*-fenchone ($[\alpha]_D^{30}$, 64°84). The following table records the properties of this ketone and its derivatives and that of fenchone and its derivatives, as described in literature.

TABLE I

	Chief fraction.	Fenchone.	Reference.
B. P.	68.5°/10 mm.	68.3/10 mm.	Miltitz, "Einfache und Fractionierte destillation", Vol. III pp. 251, 291.
Oxime m. p.	163°	163°	Mahla & Tiemann, *Ber.*, 1896, **29**, 2818.
Semicarbazone m. p.	186-187°	187°	Rimini, *Gazzetta*, 1900, **30**, 600.
2 :4-Dinitrophenylhydrazone m. p.	139–40°.	140°	Brady, *J. Chem. Soc*, 1931, 756.
$[\alpha]_D^{30}$	64° 44°	66° 54°	*Annalen*, 1941, **549**, 186.

Further confirmation was obtained by preparing derivatives from a pure sample of fenchone (isolated from the essential oil of *Blumea lacera*) and comparing their mixed m.p.

The residual solid was treated with semicarbazide hydrochloride and was made free of camphor, and the filtrate was steam-distilled; the distillate on extraction with ether and removal of the solvent gave a small quantity of a solid (m.p. 47°) appearing to be fenchyl alcohol (cf. Kenyon and Priston, *J. Chem. Soc.*, 1925, 1472). Further examination of the solid could not be done on account of meagre yield.

Experimental

Isolation of the Oil.— The essential oil was obtained by steam-distillation of dried, whole, overground plant and flowering tops from a copper still fitted with a spiral copper condenser. The steam distillate was extracted with CCl_4, the extract dried and the solvent removed on a water-bath. The greenish yellow oil, obtained (about 25-30 c. c. from 5 kg. of the material) in 0.4—0.6% yield, possesses the properties shown in the introductory part.

The oil deposited white crystals on standing and therefore it was chilled by surrounding with a freezing mixture, when a crystalline, transparent mass (12 g. approx.) was obtained. It was filtered off and recrystallised from alcohol, m. p., 178-78.5°. It sublimed even at the room temperature.

Identification of d-*Camphor*: *Semicarbazone.*—The solid (0.5 g.) was dissolved in minimum quantity of alcohol and an aqueous concentrated solution of semicarbazide hydrochloride and sodium acetate added, when crystals separated after standing the mixture for some time. The crystalline mass so obtained was filtered, dried and recrystallised from alcohol, m. p. 247-48°. Mixed m. p. with semicarbazone, prepared from a pure sample of *d*-camphor, remained undepressed.

Oxime.—To the alcoholic solution of the solid was added an aqueous solution of hydroxylamine hydrochloride, neutralised with an equivalent amount of KOH. KCl was filtered off and the mixture refluxed for 2 hours and then cooled. The oxime separating was filtered off and crystallised from alcohol, m. p. 115-16°. On recrystallisation from ethyl acetate the m. p. rose to 119°. A mixed m. p. with the oxime, prepared from a pure sample of *d*-camphor, showed no depression.

2 : 4-*Dinitrophenylhydrazone.*—A solution of 2 : 4-dinitrophenylhydrazine (0.5 g.) in H_2SO_4 (conc., 2 c.c.) and 95% alcohol (10 c.c.) was added to the solid (0.5 g.), dissolved in 10 c. c. of alcohol, and allowed to stand for some time when a yellow crystalline mass separated. It was filtered and recrystallised several times from ethyl acetate, m. p. 174-75°. Mixed m.p. determination with the derivative, prepared from a pure sample of *d*-camphor, did not show any depression.

Bromocamphor.— The ketone (0.5 g.) was dissolved in chloroform and bromine added till yellow colour persisted. After some time a crystalline mass separated which after successive recrystallisations from ethyl acetate melted at 76-77°.

Identification of d-*Fenchone.*—The liquid remaining after filtering off the camphor was fractionated, when majority of it distilled at 68.5-69°/10 mm., and the residual liquid

solidified on cooling. The main fraction was freed of camphor by treating it with a solution of semicarbazide hydrochloride and sodium acetate and filtering off the semicarbazone of camphor, so formed. The filtrate was steam-distilled and the ether extract of the distillate was dried over anhydrous sodium sulphate and the solvent distilled off. The residual liquid distilled at 68.5°/10 mm. It distilled at 192° at atmospheric pressure. (Found : C, 79.2 ; H, 10.2 ; $[\alpha]_D^{30}$, 64° 44′).

Oxime.— A solution of hydroxylamine hydrochloride (4.5 g.) and caustic potash (2.5 g.) in water (5 g.) was added to 2 c. c. of the fraction, dissolved in absolute alcohol (30 c. c.). Oxime formation took two days and the crystalline mass obtained was filtered and recrystallised several times from ethyl acetate, m. p. 163°(mixed m.p. with the oxime, prepared from a pure sample of *d*-fenchone, isolated from the essential oil of *Blumea lacera*, showed no depression).

Semicarbazone. — The fraction (2 c. c.) was dissolved in 1 c. c. of absolute alcohol and a solution of semicarbazide hydrochloride (2 g.) and sodium acetate (2 g.) in water (4 g.) was added to it. The mixture was kept at room temperature for several days when separation of a crystalline semicarbazone began after two days and took more than one week for complete separation. After successive recrystallisations from alcohol it melted at 186-87°. (Found : C, 63.2 ; H, 10.9 ; N, 19.7. Calc. for $C_{11}H_{19}O_3N$: C, 63.1 ; H, 9.0 ; N, 20.0 per cent).

2:4-*Dinitrophenylhydrazone.*— 2:4-Dintrophenylhydrazine (0.5 g.), dissolved in H_2SO_4 (conc., 2 c. c.), and alcohol (10 c. c.) was added to the fraction (1 c. c. dissolved in 10 c. c. of alcohol. On keeping the mixture overnight, a yellowish crystalline solid separated which after successive recrystallisations from ethyl acetate melted at 139-40° (sinters at 125°). (Found : C, 60.4 ; H, 6.3 ; N, 13.2. Calc. for $C_{16}H_{20}O_4N_4$: C, 60.3 ; H, 6.2 ; N, 13.3 per cent).

Mixed m. p. with the derivative obtained from a pure sample of *d*-fenchone showed no depression.

Detection of Fenchyl Alcohol.— The residual solid remaining after removal of *d*-fenchone fraction was freed of camphor in the manner described in case of the fraction containing *d*-fenchone. The purified solid after several recrystallisations from alcohol melted at 47°.

Formation of Acid Phthalate.— Phthalic anhydride was added to a small amount of the solid, dissolved in benzene, and the mixture warmed slowly for about five minutes. Excess of the anhydride was filtered off and the filtrate was neutralised with a dilute solution of sodium carbonate and then treated with dilute hydrochloric acid, when a soild separated which after several recrystallisations from alcohol melted at 145-46°.

Thanks are due to the U. P. Govt. for awarding a contingency grant and also to Dr. S. S. Deshapande for the keen interest taken in the work. Thanks are also due to Dr. A. K. Bhattacharya, Professor of Chemistry, Agra College, Agra for providing facilities for work.

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ESTIMATION OF THORIUM BY ORGANIC REAGENTS. PART VII. SEPARATION FROM CERITE EARTHS AND OTHER METALS BY *p*-AMINOSALICYLIC ACID

By Sachindra Kumar Datta and Gurupada Banerjee

Thorium has been successfully separated from the cerite earths by *p*-aminosalicylic acid from solutions having thoria : cerite-earth oxide ratio 1:13 by single precipitation, and by double precipitation when the ratio is 1 :23. Thorium can also be estimated from monazite sand; metals like U, Al, Cr, Ni, Co, Mn, Zn, Ca, Sr, Ba and Mg in moderate amounts do not interfere with the estimations.

Thorium has been determined recently, both gravimetrically and volumetrically, by *p*-aminosalicylic acid, technically known as P. A. S. (Datta and Banerjee, *Anal. Chim. Acta*, in press) within a p_H range 4 to 5.6. As the composition of the thorium salt of P. A. S. is $[(C_7H_6O_3N)\text{-}Th\text{-}(OH)_2, 3H_2O,]$ which is slightly variable in the number of associated water molecules, ignition of the precipitate to thoria is essential for its gravimetric estimation. The present paper describes methods for the separation of thorium from cerite earths and a number of common elements by this reagent. The method of separation is effective for a mixture of thorium and rare-earths, having thoria-earth oxide ratio up to 10 : 13 by single precipitation and up to 1 : 23 by double precipitation. Thorium can also be separated from a number of metal ions including uranium but metals like iron, zirconium, titanium interfere and co-precipitate with thorium.

Experimental

p-Aminosalicylic acid (B. D. H., reagent quality) was recrystallised from hot water and its 2% solution in hot water was prepared. Stock solutions of thorium, cerium, and lanthanum were prepared and their earth-contents determined as before (Datta and Banerjee, this *Journal*, 1954, **31**, 149).

Separation from Cerite Earths

Aliquot quantities of thorium-cerium or thorium-cerium-lanthanum mixtures were neutralised to Congo red and about 0.25 g. of ammonium acetate was then added. The solution was brought to boil and to it was added a hot 2% solution of P. A. S. with constant stirring till complete precipitation, and boiled for about 5 minutes more, when the precipitate became coarser. After standing for 5 minutes it was filtered, washed with 0.2% solution of the reagent and then several times with hot water, partially dried and ignited to thoria to a constant weight. The results are shown in Table I.

TABLE I

ThO_2 taken = 0.0220 g.

CeO_2.	La_2O_3.	$ThO_2:R_2O_3$.	ThO_2 by single pptn.	CeO_2.	La_2O_3.	$ThO_2:R_2O_3$.	ThO_2 by double pptn.
0.0264 g.	...	1 :1 2	0.0220 g.	0.1848 g.	0.2156 g.	1 :18.2	0.0222 g.
0.0528	0.0308 g.	1 :3.8	0.0221	0.2112	0.2464	1 :20.8	0.0221
0.0792	0.0616	1 :6.4	0.0221	0.2376	0.2772	1 :23.4	0.0223
0.1056	0.1232	1 :10.4	0 0222	0.2640	0.3080	1 :26	0 0229
0.1320	0.1540	1 :13	0.0222				
0.1320	0.1848	1 :14.5	0.0226				

It is seen from the table that the rare-earth elements do not interfere in the thorium precipitation when present in the mixture up to a thoria-earth oxide ratio of 1 : 13, beyond which a double precipitation is necessary, which could again separate thorium from the earths, up to a ratio of 1 : 23. The suitable p_H range for such separation was found to be the same, viz., 4 to 5.6, as when thorium was present alone. This fact was found out by preliminary investigations.

Separation from other Elements

The metals like Ag, Hg, Pb, Sn, etc. are also precipitated by *p*-aminosalicylic acid, and hence, thorium cannot be separated from them. The metals like Al, Zn, Co, Ni, Ca, Ba, etc. do not interfere, but double precipitation is necessary for Cr and Ni, as traces of them are held by the thorium precipitate which can only be removed by double precipitation. Zr, Ti and Fe are co-precipitated with thorium in the same p_H range, and hence, they could not be removed from thorium. Uranium does not produce any precipitate with P. A. S., but only orange colour appears. This reagent can separate thorium from uranium by single precipitation up to a $ThO_2:U_3O_8$ ratio of 1:16, beyond which double precipitation is necessary up to a ratio of 1:48. When the quantity of uranium increases beyond this ratio, it cannot be completely separated from thorium, as a small amount of it remains adsorbed in the thorium precipitate, and the ignited oxide appears coloured. The results of these separations are recorded in Tables II and III.

TABLE II

ThO_2 taken = 0.0440 g.

Oxide added.	ThO_2 found.	Oxide added.	ThO_2 found.
Al_2O_3 0 3027 g.	0.0439 g.	CaO 0.1263 g.	0.0441 g.
* Cr_2O_3 0.2134	0 0442	SrO 0.1897	0.0040
* MnO 0.1833	0.0443	MgO 0.2062	0.0441
BaO 0.2215	0.0440	ZnO 0.2342	0.0441
CoO 0 2061	0.0442	NiO 0.2781	0.0443

* Indicates double precipitation.

TABLE III

Separation of thorium from uranium.

ThO_2 taken = 0.0220 g.

U_3O_8 added.	ThO_2:U_3O_8.	ThO_2 by single pptn.	U_3O_8.	ThO_2:U_3O_8.	ThO_2 by double pptn.
0.0900 g.	1 : 4.1	0.0220 g.	0.5400 g.	1 : 24.6	0.0223 g.
0.1800	1 : 8.2	0.0222	0.7200	1 : 32.8	0.0224
0.2025	1 : 9.2	0.0221	0.8100	1 : 36.8	0.0224
0.2700	1 : 12.3	0.0222	1.0800	1 : 48.8	0.0226
0.3600	1 : 16.4	0.0223			
0.4050	1 : 18.4	0.0230			

Extraction of Thorium from Monazite Sands.

Zirconium-free extracts of monazite sand (Travancore and Brazilian sands), prepared by the usual method (Raghava Rao, *et al.*, this *Journal*, 1950, **27**, 458) were neutralised to Congo red and thorium was precipitated from them as before by this reagent, after adding a small amount of ammonium acetate. It was found that thorium could be separated from these extracts by a single precipitation. The results have been compared with those obtained by *m*-nitrobenzoic acid (Table IV).

TABLE IV

Estimation of thorium from Monazite sands.

Wt. of the sample.	P. A. S. ThO_2 obtained.	P. A. S. % ThO_2.	*m*-Nitrobenzoic acid. ThO_2 obtained.	*m*-Nitrobenzoic acid. % ThO_2.
Indian Monazite.				
0.5620 g.	0.0411 g	7.32	0.0412 g.	7.32
1.1340	0.0829	7.31	0.0829	7.31
1.2759	0.0934	7.32	0.0933	7.31
Brazilian Monazite.				
1.0683	0.0481	4.50	0.0480	4.49
1.2194	0.0548	4.49	0.0549	4.50
1.6857	0.0759	4.50	0.0759	4.50

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IONIC EQUILIBRIA IN SOLUTION. PART IV. LEAD PROPIONATE IN AQUEOUS SOLUTION

By Radha Charan Mohanty and S. Aditya

The nature of lead propionate in solution has been studied by the measurement of solubility of lead iodate in sodium propionate solution and also by E. M. F. measurement of the concentration cells of the type, $Pb_x\ Hg_y\ |\ Pb(NO_3)_2 \| \text{salt bridge} \| NaPr\text{-}Pb(NO_3)_2\ |\ Pb_x\ Hg_y$ at 35°.

The equilibrium in solution can be represented as

$$\begin{array}{ccc} PbPr_2 & \underset{K_1}{\rightleftharpoons} & PbPr^+ + Pr^- \\ & & \uparrow\downarrow K_2 \\ & & Pb^{2+} + Pr^- \end{array}$$

The mean value of K_1 is 3.1×10^{-2} and that of K_2 is 2.2×10^{-3}.

The nature of lead acetate in aqueous solution has been investigated by several workers (cf. this *Journal*, 1952, **29**, 169). Literature, however, does not record any investigation of the physicochemical properties of lead propionate in solution. It is very likely that lead propionate, being the salt of a homologue of acetic acid, might show similar behaviour. The similarity in the nature of copper carboxylates in solution has been reported by Miss Lloyd *et al.* (*J. Chem. Soc.*, 1951, 1786).

The nature of lead propionate in solution has been investigated by finding out the solubility of lead iodate in sodium propionate and the conclusion thereof has been confirmed by analysis of the data from the E. M. F. measurements of suitable concentration cells.

Experimental

Lead iodate was prepared in the same way as described by La Mer and Goldman (*J. Amer. Chem. Soc.*, 1930, **52**, 2791).

Sodium propionate solution having the required p_H was prepared by mixing propionic acid (Merck, EP) and sodium hydroxide solutions of known strengths. The p_H was checked by the Marconi p_H meter.

The solubility of lead iodate in sodium propionate solution was determined at 35° by taking lead iodate in sodium propionate solution of proper concentration, shaking and equilibrating. The filtered solution was analysed for the iodate content by titrating with $N/20$ thiosulphate solution which in turn was standardised against standard iodate. The solubility data of $Pb(IO_3)_2$ in sodium propionate at p_H 4.7 and 5.7 are shown in columns 3 of Tables I and II.

TABLE I

Solubility of lead iodate in sodium propionate solution.
(Salt : acid = 10:1).

Conc. of salt.	log s_o in KNO_3	log s in NaPr.	log s^3_o/s^2.	log $(s-s^3_o/s^2)$.	log $f_{Pb^{2+}}$.	$K_2\times10^3$.	$K_1\times10^2$.
0.01*M*	$\bar{5}.8175$	$\bar{4}.0017$	5 4490	$\bar{5}.8593$	$\bar{1}.8325$	2.62	...
0.02	$\bar{5}.8500$	$\bar{4}.1183$	$\bar{5}.3135$	$\bar{4}.0444$	$\bar{1}.7482$	2.06	...
0.04	$\bar{5}.8900$	$\bar{4}.2514$	$\bar{5}.1873$	$\bar{4}.2133$	$\bar{1}.6532$	1.61	5.02
0.06	$\bar{5}.9200$	$\bar{4}.3412$	$\bar{5}.0778$	$\bar{4}.3168$	$\bar{1}.5798$	1.31	4.16
0.08	$\bar{5}.9500$	$\bar{4}.4074$	$\bar{5}.0341$	$\bar{4}.3885$	$\bar{1}.5441$	1 26	5.33
0 10	$\bar{5}.9717$	$\bar{4}.4623$	$\bar{6}.9868$	$\bar{4}.4476$	$\bar{1}.4983$	1.12	5.44
0 12	$\bar{4}.0017$	$\bar{4}$ 5045	$\bar{6}.9959$	$\bar{4}$ 4907	$\bar{1}.4472$	1.07	6.56
0.15	$\bar{4}.0417$	$\bar{4}.5167$	$\bar{5}.0319$	$\bar{4}.5333$	$\bar{1}.4150$	1.23	9.16
0.20	$\bar{4}.0835$	$\bar{4}.6427$	$\bar{6}.9638$	$\bar{4}.6070$	$\bar{1}.3222$	0.97	7.16

Extrapolated value of $K_2 = 2.2\times10^{-3}$.
Mean value of $K_1 = 6.2\times10^{-2}$.

TABLE II

Solubility of lead iodate in sodium propionate solution.
(Salt : acid : 1: 1).

Conc. of salt	log s_o in KNO_3.	log s in NaPr.	log s_o^3/s^2.	log $(s-s_o^3/s^2)$.	log $f_{Pb^{2+}}$.	$K_2\times10^3$.	$K_1\times10^2$.
0.01*M*	$\bar{5}.8175$	$\bar{5}.9930$	$\bar{5}$ 4664	$\bar{5}.8396$	$\bar{1}.8325$	2.18	...
0.02	$\bar{5}.8500$	$\bar{4}.1239$	$\bar{5}.3021$	$\bar{4}.0531$	$\bar{1}.7482$	1.99	...
0 04	$\bar{5}.8000$	$\bar{4}.2427$	5 1847	$\bar{4}.2031$	$\bar{1}.6532$	1.73	9.67
0.06	$\bar{5}.9200$	$\bar{4}.3683$	$\bar{5}.0233$	$\bar{4}.3483$	$\bar{1}.5798$	1.08	3.74
0.08	$\bar{5}$ 9500	$\bar{4}$ 3934	$\bar{5}.0633$	$\bar{4}.3726$	$\bar{1}.5441$	1.37	8.21
0 12	$\bar{4}.0017$	$\bar{4}.4895$	$\bar{5}.0261$	$\bar{4}.4742$	$\bar{1}.4472$	1.20	7.19
0 15	$\bar{4}.0417$	$\bar{4}.5446$	$\bar{5}.0359$	$\bar{4}$ 5308	$\bar{1}.4150$	1.25	9 89
0.20	$\bar{4}.0915$	$\bar{4}.6033$	$\bar{5}.0453$	$\bar{4}$ 5912	$\bar{1}.3222$	1.19	11.97

Extrapolated value of $K_2 = 2.2\times10^{-3}$.
Mean value of $K_1 = 8.4\times10^{-2}$.

In the subsequent study by the E. M. F. method, the cells of the type

$$Pb_x\ Hg_y \mid Pb(NO_3)_2 \parallel \underset{NaPr}{} \parallel Pb(NO_3)_2 \mid Pb^x\ Hg_y$$

were set up and the E. M. F. was measured by means of the Tinsley Vernier potentiometer at 35°. The cell vessels and the bridge solution (saturated ammonium nitrate) were similar to those used in the previous work (this *Journal*, 1951, **28**, 683).

All the settings were done in duplicate. The mean E. M. F. readings are recorded in column 3 of Table III.

TABLE III.

Cell: $Hg, Pb_x\ Hg_y \mid Pb(NO_3)_2\ (c),\ NaPr\ (c') \parallel$ salt bridge $\parallel Pb(NO_3)_2\ (c) \mid Pb_xHg_y, Hg.$

Conc. of $Pb(NO_3)_2$	Conc. of NaPr.	Mean E.M.F.	Activity of Pb^{2+}.	β.	$K_2 \times 10^3$.	* $K_1 \times 10^2$.
0.01*M*	0.02*M*	0.0181 mv.	0.0012	0.2688	2.17	...
0.01	0 03	0.0256	0 0007	0.1598	1.83	4 76
0.01	0.04	0.0305	0.0005	0.1168	1.73	5.44
0.02	0 04	0.0229	0.0014	0.1880	2.05	3.32
0.02	0.06	0.0320	0.0007	0.1042	1.67	3.72
0.02	0.08	0.0397	0 00 4	0.0630	1.30	3.09
0.03	0.06	0.2640	0.0013	0.1413	1.80	1.78
0.03	0.09	0 0369	0.0006	0.0743	1.49	2.50
0.03	0.12	0 0424	0.0004	0.0518	1.30	3.95
0.04	0.08	0 0284	0.0014	0 1250	1 71	1.00
0 04	0 12	0.0401	0.0005	0.0525	1.23	1.00
0.05	0.10	0.2965	0.0014	0.1130	1 76	0 79

* Based on $K_2 = 2.2 \times 10^{-3}$. Mean 0.30

DISCUSSION

The solubility of lead iodate in solution containing sodium propionate at p_H 5.9 (where the ratio of sodium propionate to propionic acid was 10:1) is shown in Table I and that at p_H 4.7 (ratio 1:1) in Table II. The solubility of lead iodate at the two p_H regions is the same within the experimental error. This indicates that the equilibrium is independent of p_H within this range. The solubility of lead iodate in a solution of potassium nitrate having the same concentration as sodium propionate is also shown in the tables (column 2) for comparison. If the variation of solubility of lead iodate in potassium nitrate is taken to be due to variation in ionic strength of the solution, the higher solubility of lead iodate in sodium propionate must be due to the interaction of the propionate ion with lead ion. The ion-complex formation may be represented in the following way:

$$Pb(IO_3)_2 + n\ Pr^- \rightleftharpoons PbPr_n^{-n+2} + 2IO_3^-$$

The equilibrium constant will be given by the equation,

$$K = \frac{(Pb^{2+})\ (Pr^-)^n}{(PbPr_n)^{-n+2}}, \quad \text{where } (\quad) \text{ signifies activity.}$$

Putting concentration in place of activity, *i.e.*, neglecting ionic attraction terms for preliminary analysis,

$$K = \frac{[Pb^{2+}]\ [Pr^-]^n}{[PbPr_n]^{-n+2}} \quad \text{where } [\quad] \text{ signifies concentration.}$$

Now, $[Pb^{2+}] = s'_0{}^2/s^2$ where s'_0 is the solubility in water (zero concentration of propionate) and 's' is the solubility in sodium propionate solution.

$$[PbPr_n)^{-n+2}] = s - \frac{s_o^3}{s^2}.$$

The concentration of $[Pr^-]$ can be taken to be equal to the initial concentration of sodium propionate. Taking the logarithims we have

$$n \log [Pr^-] = \log [PbPr_n{}^{-n+2}] - \log [Pb^{2+}] + \log K.$$

On plotting $\log [Pr^-]$ against $\log [PbPr_n{}^{-n+2}] - \log [Pb^{2+}]$ we get a straight line, from the slope of which the value of $1/n$ is found to be nearly 0.5. This indicates that two propionate ions are associated with a single Pb^{2+} ion. The slope is not exactly 0.5 as both $PbPr_2$ as well as $PbPr^+$ will be present.

Assuming then that the ion association takes place to the extent of $PbPr_2$, the two stages of equilibrium may be represented as

$$PbPr_2 \rightleftarrows PbPr^+ + Pr^-$$

$$\uparrow\downarrow$$

$$Pb^{2+} + Pr^-$$

Hence, $$K_2 = \frac{(Pb^{2+})\,(Pr^-)}{(PbPr^+)}$$, and

$$K_1 = \frac{(PbPr^+)\,(Pr^-)}{(PbPr_2)} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

The two dissociation constants have been evaluated in the following manner. At first it is assumed that Pb^{2+} combines with Pr^- to give only $PbPr^+$, *i.e.*, the dissociation of $PbPr_2$ into Pb^{2+} and Pr^- is complete. The activity of (Pb^{2+}) ion, $cf_{Pb^{2+}}$, (c being concentration of Pb^{2+}), has been calculated as follows. In sodium propionate solution, $(Pb^{2+}) \times (IO_3^-)^2 f_{Pb^{2+}} \times f^2_{IO_3^-} = s$ (solubility product). If the solubility of lead iodate in solution and of potassium nitrate and sodium propionate having the same concentration be s_o and s, then,

$$s^3{}_o/s^2 = (Pb^{2+}).$$

Since the solubility is quite low, the ionic strength of both the solutions may be taken to be equal; in other words, the activity coefficient terms will be equal. Therefore,

$$(Pb^{2+}) = \frac{s^3{}_o/s^2}{s^2} \quad \text{and}$$

$$(PbPr^-) = s - s^3{}_o/s^2.$$

Of course, the above value of $(PbPr^+)$ will be slightly higher than the true concentration of $PbPr^+$, since

$$(Pb^{2+})_{Total} = (Pb^{2+}) + (PbPr^+) + (PbPr_2).$$

The difference will be greater, the greater the concentration of sodium propionate, and hence of $PbPr_2$. However, as a first approximation, $(PbPr^+)$ has been taken to be equal to $(s - s_o{}^3/s^2)$. The concentration of Pr^- has been taken to be equal to that of sodium propionate. The activity coefficient of Pb^{2+} has been calculated in the same way as has been done in a communication by Prasad, Aditya *et al.* (this *Journal*, 1951, **28**, 683).

Having known $f_{Pb^{2+}}$, the value of K_2 has been calculated from the expression:

$$K_2 = \frac{[s^3_o/s^2]\,[NaPr]}{[s - s^3_o/s^2]} f_{Pb^{2+}},$$

which is obtained from equation (1) on simplification, assuming $f_{PbPr^+} = f_{Pr^-}$. The values of K_2 given in column 7 of the table show a decrease as the concentration of sodium propionate increases. That is what is expected from the above considerations, for as (NaPr) becomes higher, ($PbPr^+$) that we have used becomes actually greater than its true value. A true value of K_2 has been obtained by extrapolating the value of K_2 plotted against c, which comes out to be 2.2×10^{-3}. With this value of K_2, K_1 has been calculated in the following way.

If α and β are the degrees of dissociation for the two ionic equilibria in lead propionate in aqueous solution, we have, taking $f_{Pr^-} = f_{PbPr^+}$,

$$K_1 = \frac{(PbPr^+) \times (Pr^-)}{(PbPr_2)} \text{ and } K_2 = \frac{(Pr^-)\,(Pb^{2+})}{(1-\beta)\alpha c} f_{Pb^{2+}}$$

Let $(Pr^-) = c'$ and $\alpha\,\beta\,c = A$, then

$$K_2 = \frac{c'\,A f_{Pb^{2+}}}{\alpha c - A.} \quad \text{or} \quad \alpha = \frac{A\,(c'\,f_{Pb^{2+}} + K_2)}{K_2 c}.$$

Now substituting the values of K_2, c', $f_{Pb^{2+}}$ and c (the solubility of lead iodate), α has been calculated. Now α being known, β can be calculated. With the values of α and β, K_1 has been calculated using the equation,

$$K_1 = \frac{(PbPr^-_{(2)})\,f_{PbPr^+}\,(Pr^-)\,f_{Pr^-}}{(PbPr_2)} = \frac{(1-\beta)\,\alpha c\,[Pr^-]\,f^2_{Cl^-}}{(1-\alpha)\,c},$$

assuming $f_{PbPr^+} = f_{Pr^-}$ and each of these being equal to f_{Cl^-} at the same ionic strength. Column 8 of Tables I and II gives the value of K_1 the mean of which is 7×10^{-2}.

For the purpose of analysis of the results obtained by the E. M. F. method we have, for the cell described above,

$$E = \frac{RT}{2F} \ln \frac{c f_{Pb^{2+}}}{c' f'_{Pb^{2+}}} + e,$$

where $c f_{Pb^{2+}}$ and $c' f'_{Pb^{2+}}$ represent activity coefficient of lead ion in the solution in the two half elements and e, the liquid junction potential.

Assuming that the junction potential is eliminated for all practical purposes, the E.M.F. will be a function of ionic strength of the solution in the two half cells, since the concentrations of lead ions are equal. The fact that the observed E.M.F. is much greater than what can be accounted for by the ionic strength, leads us to assume interaction between Pb^{2+} and Pr^- ions. The solubility results also support this assumption.

For the concentration cell studied, we have,

$$E = \frac{RT}{2F} \ln \frac{c f_{Pb^{2+}}}{a_{Pb^{2+}}}$$

where $a_{Pb^{2+}}$ is the activity of Pb^{2+} ions in a mixture of $Pb(NO_3)_2$ and NaPr and $c f_{Pb^{2+}}$ is the activity of Pb^{2+} ions in $Pb(NO_3)_2$ solution.

Assuming lead nitrate to be completely dissociated, $a_{Pb^{2+}}$ has been calculated. The values of $a_{Pb^{2+}}$ which is equal to $\alpha\beta c f_{Pb^{2+}}$ are shown in column 4 of Table III. These values are then used to calculate K_1 and K_2 by the approximation method.

It was pointed out in a previous paper (this *Journal*, 1953, **30**, 213) that so far as the calculation of K_2 is concerned, we can assume without making any great error, that the first stage of dissociation is complete, *i.e.*,

$$PbPr_2 \longrightarrow PbPr^+ \rightleftharpoons Pb^{2+} + Pr^-.$$

Then following the same method as was done in the case of lead acetate (*loc. cit.*), the values of K_2 for different ionic strengths were calculated.

Depending on the ratio of concentration of $Pb(NO_3)_2$ to NaPr the equations used were :

$$K_2 = \frac{(1+\beta)}{(1-\beta)}\, a_{Pb^{2+}}, \text{ where the ratio is 1:2;}$$

$$K_2 = \frac{2+\beta}{1-\beta}\, a_{Pb^{2+}}, \text{ where the ratio is 1:3;}$$

$$K_2 = \frac{3+\beta}{1-\beta}\, a_{Pb^{2+}}, \text{ where the ratio is 1:4.}$$

The values of K_2 calculated in this manner are recorded in column 6 of Table III. Plotting log K_2 against c, the extrapolated value of K_2 is found to be 2.2×10^{-3}. Taking this value of K_2, that of K_1 has been calculated in the following way.

In the cases where the ratio of $Pb(NO_3)_2$ to NaBr is 1:2 we have,

$$K_1 = \frac{(1-\beta)\alpha\, cf_+}{(1-\alpha)} \frac{(1+\beta)\alpha f_-}{} \quad \text{and}$$

$$K_2 = \frac{(1+\beta)}{1-\beta} \times A\, f_{2+},$$

where $A = \alpha\beta\, c$ and f_{2+} f_+, and f_- are the activity coefficients of Pb^{2+}, $PbPr^+$ and Pr^- respectively. From the second equation,

$$\beta = \frac{(K_2/f_{2+} - A)}{A + K_2/f_{2+}}.$$

The ionic strength of the solution is given by the relation

$$\mu = c(\alpha + 2\alpha\beta) + 2c.$$

K_2 being known, the values of β and μ have been calculated by the method of successive approximation till a constant value of β is obtained. With this value of β, K_1 is evaluated assuming the activity of the same valence type ion to be the same in solution having the same ionic strength.

The values of β and K_1, calculated in a similar manner for the case where ratio of $Pb(NO_3)_2$ to NaPr is 1:3, are shown in columns 5 and 7 of Table III. The mean value of K_1 is 3.1×10^{-2}.

While comparing the values obtained by the two methods, we find that K_2 is 2.2×10^{-3} by both the methods. But the value of K_1 is 3.1×10^{-2} by E.M.F. and 7×10^{-2} by the solubility method. It must be noted that in the latter method large approximations have been used in the calculation.

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HYDROXYFLUOBERYLLATES. PART I

By Grihapati Mitra

The substitution of a hydroxyl group for fluorine atom in the fluoberyllate ion results in the formation of the hydroxyfluoberyllate ion. The methods of preparation and propreties of the hydroxyfluoberyllates of the alkali metals and ammonia have been discussed. The thermometric titration of potassium fluoberyllate bv sodium hydroxide gives a break which corresponds to the formation of the hydroxyfluoberyllate. The hydroxyfluoberyllates of the alkali metals are in general more soluble than the fluoberyllates, and some of the compounds are deliquescent. The ammonium hydroxyfluoberyllate serves as a better starting material for the preparation of NH_4BeF_3. From a theoretical consideration it has been shown that the hydroxyfluoberyllates should remain isoelectronic and isosteric with the sulphates, and this fact has been proved both from the chemical nature of the compounds and by X-ray analysis.

Double fluorides of beryllium were studied first by Marignac (*Ann. chim. phys.*, 1873, *iv*, **30**, 45). A systematic study on the chemistry of the fluoberyllates was, however, made by N. N. Ray (*Z. anorg. Chem.*, 1931, **201**; 1932, **205**, 257; 1936, **227**, 32, 103).

It was observed by many workers previously that beryllium hydroxide dissolved in beryllium fluoride. Boron, too, the immediate horizontal neighbour of beryllium in the Periodic Table, has been found to yield complex hydroxyfluorides (Meerwein, *Ber.*, 1933, **66**, 411; *Annalen*, 1927, **227**, 455; Meerwein and Pannwitz, *J. parkt. Chem.*, 1934, **141**, 123). The rate of reaction and hydrolysis constant of the complex fluorides of boron reveal that the reaction,

$$H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O,$$

is instantaneous. This hydroxyfluoborate reacts slowly and only in presence of excess of hydrofluoric acid to furnish the tetrafluoborate (cf. Wamser, *J. Amer. Chem. Soc.*, 1948, **70**, 1209)

$$HBF_3OH + HF \longrightarrow HBF_4 + H_2O.$$

This stepwise introduction of fluorine atom and the existence of the intermediate hydroxyfluoride complex have also been recognised in the case of the fluophosphates (Lange, *Ber.*, 1929, **62**, 786). In view of these observations it was considered of interest to explore the possibility of the existence of the hydroxyfluoride complexes of beryllium. In fact, their formation might be assumed from the following considerations:

The Be—O linkage in the solid stage is 63% ionic in character. It has been shown by Pauling that BeO has a Wurtzite (4:1) lattice indicating the presence of a co-valent linkage in the solid state. As it has been found that in a co-ordinate linkage the distance between the donor atom and the acceptor is in general between ionic and co-valent, it suggests, so far as the nature of linkage is concerned, that beryllium can form complex

anions with oxygen as a donor. In fact, the complex anion of the type BeO_2^{2-} is already known.

Tananaev and Deichman (*Bull. Acad. Sci. USSR.*, 1947, 591 ; Otdel, *Khim. Nauk*, 1949, 144), have shown that in a saturated solution of beryllium hydroxide in beryllium fluoride the ratio of $Be(OH)_2$: BeF_2 is 1 : 3.5. The present worker has, however, found that in a very concentrated solution of beryllium fluoride a larger amount of beryllium hydroxide goes into solution. If cold water be added to this solution, beryllium hydroxide is, however, precipitated and the final stable solution contains beryllium fluoride and beryllium hydroxide in the proportion of 3 : 1. This is in accord with the following reaction :

$$3BeF_2 + Be(OH)_2 = 2Be(BeF_3OH).$$

Addition of alkali to solutions of fluoberyllates of Ni, Co, Cu, etc. affords no precipitate to begin with. The hydroxides appear only after the addition of an excess of alkali. This can be accounted for by the following reaction :

$$M\,BeF_4 + KOH = M\,BeF_3OH + KF.$$

A solution of the fluoberyllate shows a p_H value in the acidic range, indicating the presence of hydrofluoric acid resulting from hydrolysis with the formation of hydroxyfluoberyllate

$$H_2O + BeF_4^{2-} \longrightarrow BeF_3OH^{2-} + HF.$$

All attempts to isolate the fluoberyllates of metals that form insoluble fluorides (e.g. rare-earth metals, Mg, Mn, etc.) ended in failures. It has, however, been noticed that the precipitates formed by the addition of ammonium fluoberyllate to the solution of the nitrates of these metals always contain a sufficient amount of beryllium. As both the nitrate and fluoride of beryllium are highly solubie in water, the existence of beryllium in the precipitate can only be accounted for on the assumption of a complex hydroxyfluoride as shown below.

$$2Ce(NO_3)_3 + 3(NH_4)_2\,BeF_4 = Ce_2(BeF_4)_3 + 6NH_4NO_3$$
$$Ce_2(BeF_4)_3 + 3H_2O = Ce_2(BeF_3OH)_3 + 3HF$$
$$Ce(NO_3)_3 + 3HF = CeF_3 + 3HNO_3$$

The precipitate, however, is never a mixture of the equimolecular quantities of insoluble fluoride and hydroxyfluoberyllate for various reasons. Nitric acid, for example, is formed as a result of this reaction and it breaks BeF_3OH^{2-} ion partially, as a result of which further precipitation of insoluble fluorides occurs.

The strong tendency of beryllium to form complexes with four donors at the corners of a regular tetrahedron has been recognised from various studies. In a hydroxyfluoberyllate anion therefore, the three fluorine atoms and the hydroxyl group occupy the corners of the regular tetrahedron with the beryllium atom at the centre. If we study the stability of the two groups, fluoberyllate and the hydroxyfluoberyllate, from a purely theoretical standpoint, we find that as the polarisability of oxygen is greater than that of fluorine (the values being 3.1 and 0.99 units respectively), the hydroxyfluoberyllate group should be more stable than the other. This fact has been supported from

certain other aspects. Hydroxyfluoberyllate, for example, affords organic compounds like ethyl hydroxyfluoberyllate, while no ethyl fluoberyllate is known. It may be mentioned in this connection that the partial replacement of chlorine by hydroxyl group in certain chloro complexes has been found to increase the stability of the complex (Scholder and Patsch, *Z. anorg. Chem.*, 1934, **217**, 214).

The ionic radii of fluorine and hydroxyl group are 1.33 Å and 1.4 to 1.5 Å respectively. As substitution of a hydroxyl group inside the complex for a fluorine atom makes no appreciable difference in the crystal lattice, the hydroxyfluoberyllate and the fluoberyllate ions should remain isomorphous. Although the hydroxyl ion is slightly greater in size than that of the fluorine ion, the difference is compensated by the increased co-valent character of Be—O bond compared to that of Be—F linkage and by the increased polarisability of the hydroxyl ion over that of the fluorine ion.

X-ray analysis confirms the isomorphism of the hydroxyfluoberyllates with the fluoberyllates and the sulphates. Similar observations have also been made by Kilkenberg and Ketelaar in the case of the fluoborates and the hydroxyfluoborates (*Rec. trav. chim.*, 1935, **54**, 959 ; 1937, **56**, 36).

Experimental

Method of Analysis.—The alkali metals were estimated as their sulphates after the separation of beryllium. Ammonia was determined by the Kjeldahl method. The amount of beryllium was determined as beryllium oxide after removal of the fluorine. Fluorine was estimated both as calcium fluoride and as lead chlorofluoride.

Thermometric Titration of Potassium Fluoberyllate.—The titration of a solution of potassium fluoberyllate by a concentrated solution of sodium hydroxide gave a break which corresponded to the formation of hydroxyfluoberyllate.

Potassium fluoberyllate (1.1923 g.) was dissolved in the minimum quantity of water and titrated with a solution of 2.9223*N*-NaOH. All relevant precautions were taken. The temperature was noted with a Beckmann thermometer after the addition of each 0.5 c.c. aliquot of NaOH solution. Results are shown in Table I.

Table I

No.	NaOH added.	Beckmann reading.	No.	NaOH added.	Beckmann reading.	No.	NaOH added.	Beckmann reading.
1.	0.55 c.c.	0.438	6.	3.0 c.c.	0.426	10.	5.0 c.c.	0.420
2.	1.0	0.438	7.	3.5	0.420	11.	5.5	0.018
3.	1.5	0.438	8.	4.0	0.420	12.	6.0	0.012
4.	2.0	0.438	9.	4.5	0.420	13.	6.5	0.014
5.	2.5	0.438				14.	7.0	0.012

The formation of hydroxyfluoberyllate is responsible for the first break while the second break is due to the complete precipitation of beryllium hydroxide.

$$K_2BeF_4 + NaOH = K_2BeF_3OH + NaF \text{ (1st break)}$$
$$K_2BeF_3OH + NaOH = Be(OH)_2 + 2KF + NaF \text{ (2nd break)}$$

The alkali salts of the complex fluoride anions are peculiar in certain respects. The salts are undoubtedly ionic in nature, but still, their solubilities are surprisingly low. The number of water molecules attached to them has been found to be peculiar. Sodium and potassium salts of the pentafluoferriate, for example, crystallise with ½ or 1 molecule of water. The method of preparation and properties of the hydroxyfluoberyllates of alkali metals and ammonia are discussed below.

General Methods of Preparation

(*a*). A weighed quantity of carbonate of the alkali metal was taken in a platinum basin. A known volume of a concentrated solution of the alkali hydroxide may also be taken. Slightly excess than the theoretical amount of freshly precipitated beryllium hydroxide was then added to it followed by the addition of 75 c.c. of water. The mixture was heated on a water-bath. 20% Hydrofluoric acid solution was then added to it at intervals. When the solution became just turbid due to the presence of last traces of unchanged beryllium hydroxide, the addition of HF was stopped. The digestion on the water-bath should be carried out at least for 45 minutes to ensure complete hydrolysis. The alkali salts were obtained from this solution. The sparingly soluble hydroxyfluoberyllates of Na and K were precipitated in the form of colorless crystals during the time of preparation. For the preparation of other salts, however, the concentrated solutions had to be kept in a vacuum desiccator. The ammonium salt was crystallised out in an atmosphere of ammonia.

(*b*). Equimolecular quantities of beryllium hydroxide, alkali metal fluoride and alkali metal bifluoride may also serve as the starting materials for the preparation of these salts. The mixture was taken in a platinum basin and heated on a water-bath. Theoretically, the addition of hydrofluoric acid is not nesessary, but in actual practice it has always been found that some amount of hydrofluoric acid from acid fluoride escapes the reaction, and so a few drops of hydrofluoric acid should be added.

(*c*). The sparingly soluble alkali metal hydroxyfluoberyllates are obtained by adding the corresponding alkali nitrate solution to a moderately dilute solution of copper hydroxyfluoberyllate. The concentrated solution of Cu-hydroxyfluoberyllate should not be used because in the latter case some amount of the double hydroxyfluoberyllate is formed.

The alkali metal hydroxyfluoberyllates were generally washed at first with cold water and then with 60% alcohol and finally dried in a vacuum desiccator. The following compounds were prepared.

(1) *Lithium hydroxyfluoberyllate*: (Found: Li, 14.32; F, 59.32. Li_2BeF_3OH requires Li, 14.31; F, 58.76 per cent).

(2) *Sodium hydroxyfluoberyllate*: (Found: Na, 34.49; F, 43.44. Na_2BeF_3OH requires Na, 35.66; F, 44.19 per cent).

(3) *Potassium hydroxyfluoberyllate*: (Found: Be, 5.53; F, 35.39. K_2BeF_3OH requires Be, 5.54; F, 35.40 per cent).

(4) *Rubidium hydroxyfluoberyllate*: (Found. Rb, 66.85; F, 22.35. Rb_2BeF_3OH requires Rb, 67.35; F, 22.45 per cent).

(5) *Ammonium hydroxyfluoberyllate*: [Found: Be, 7.62; F, 48.58; NH_3, 29.80. $(NH_4)_2BeF_3OH$ requires Be, 7.58; F, 47.90; NH_3, 30.25 per cent].

Properties

The hydroxyfluoberyllates of the alkali metals are more soluble than the corresponding fluoberyllates. The substitution of the hydroxyl group in place of the fluorine atom, in general, increases the solubility of the salt, and similar observation has already been made in connection with the hydroxyfluoborates (*loc. cit.*). These hydroxyfluoberyllates like the hydroxyfluoborates cannot be recrystallised from water. Lithium hydroxyfluoberyllate is easily hydrolysed in solution and a mixture of insoluble fluoride and hydroxide of lithium is precipitated. The hydrated salts of the hydroxyfluoberyllates of the alkali metals could not be prepared. By heating the sodium salt no compound of the type $Na_2BeF_3O\text{-}BeF_3Na_2$ could be prepared. A similar compound has, however, been described in connection with sodium hydroxyfluostannate. The sodium and potassium hydroxyfluoberyllates are sparingly soluble in water; the lithium hydroxyfluoberyllate is difficult to prepare, while the other hydroxyfluoberyllates are highly soluble.

The p_H value of a saturated solution of potassium hydroxyfluoberyllate has been found to be nearly 7, while that of a potassium fluoberyllate solution is nearly 5.

Most of the hydroxyfluoberyllates are deliquescent in nature. The alkali hydroxyfluoberyllates may be safely heated to a high temperature. Ammonium hydroxyfluoberyllate, when perfectly dry, is stable under ordinary conditions, a little warming, however, decomposes the salt. Thus, ammonium hydroxyfluoberyllate starts as a better starting material than ammonium fluoberyllate for the preparation of NH_4BeF_3. Ammonium fluoberyllate is very stable and serves as the starting material for the preparation of all other fluoberyllates. The ammonium hydroxyfluoberyllate, on the other hand, is not so stable. If a solution of ammonium hydroxyfluoberyllate be heated, gaseous ammonia is evolved and the solution gradually becomes rich in fluoberyllate content. Accidentally the ammonium fluoberyllate was chosen as the starting material for the preparation of all other fluoberyllates, and now it is being found that this ammonium fluoberyllate has the least possibility for being in contamination with the hydroxyfluoberyllate.

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HYDROXYFLUOBERYLLATES. PART II. HYDROXYFLUOBERYLLATES OF Ca, Ba, Sr, Pb, Ce, La, AND Hg

By Grihapati Mitra

The preparation and properties of some of the insoluble and sparingly soluble hydroxyfluoberyllates have been described. The hydroxyfluoberyllate of calcium, barium, strontium and lead were prepared by the double decomposition between the nitrates of these metals and a soluble hydroxyfluoberyllate like the nickel hydroxyfluoberyllate. Lanthanum and cerium hydroxyfluoberyllates were prepared by the action of ammonium hydroxyfluoberyllate on the nitrates of these metals in presence of traces of amyl alcohol. The basic hydroxyfluoberyllate of mercury was also prepared. The fluoberyllates of Ce, La and Hg have not been isolated as yet. Some of these hydroxyfluoberyllates are deliquescent in nature. These hydroxyfluoberyllates are more soluble than the corresponding fluoberyllates. The X-ray diffraction diagram of the barium salt reveals that it is isomorphous with the corresponding sulphate.

It has been theoretically shown in the previous communication (this *issue*, p. 241) that from certain points of view the hydroxyfluoberyllate ion should behave as a more stable ion than the fluoberyllate ion. This fact has been proved experimentally in this paper. The fluoberyllates of Ce, La and Hg have not yet been isolated. Owing to the secondary dissociation of the fluoberyllate radical, the fluoride ions are formed in solution resulting in the precipitation of the insoluble fluorides. The hydroxyfluoberyllates of Ce and La have, on the other hand, been isolated in the form of beautiful crystals. The basic hydroxyfluoberyllate of Hg has also been prepared.

Experimental

The rare-earth metals were precipitated as their oxalates and finally estimated as oxides. The amount of fluorine was determined as lead chlorofluoride or calcium fluoride. The usual methods of analysis were followed for the estimation of other elements. Presence of Be in all the compounds described was determined qualitatively.

Calcium Hydroxyfluoberyllate.—Much difficulties were experienced by previous workers in preparing calcium fluoberyllate. It can be prepared by fusing calcium chloride with ammonium fluoberyllate. The mass left after fusion contains calcium fluoberyllate mixed with calcium fluoride. Calcium fluoride is removed by boiling the resulting mass with glacial acetic acid. The hydroxyfluoberyllate was prepared, however, more easily by the following method.

A few drops of amyl alcohol was added to a very concentrated solution of ammonium hydroxyfluoberyllate, cooled with ice and salt, and a cold concentrated solution of calcium chloride was added to it, when a very fine white precipitate was formed. It was filtered and dried in a desiccator. (Found: Ca, 32.33; F, 46.42. $CaBeF_3OH$ requires Ca, 32.56 ; F, 46.31 per cent).

The dihydrated form of calcium hydroxyfluoberyllate could not be isolated. The dihydrated compound, even, if formed, loses two molecules of water quickly over

sulphuric acid. Calcium hydroxyfluoberyllate is perfectly crystalline under the microscope.

Strontium hydroxyfluoberyllate was prepared by double decomposition between solutions of strontium nitrate and ammonium hydroxyfluoberyllate, cooled to 0°. At first a gummy mass was obtained, which on brisk stirring disintegrated yielding a white powdery substance. Sufficient heat was evolved and the temperature of the mixture was not allowed to rise much. The precipitated substance was filtered and washed with cold water for four or five times. It was finally washed with alcohol and dried at 80°. (Found : Sr, 50.58 ; F, 33.28. $SrBeF_3OH$ requires Sr, 51.36 ; F, 33.41 per cent). Strontium hydroxyfluoberyllate is a fine white crystalline powder, sparingly soluble in water.

Barium hydroxyfluoberyllate was prepared by the double decomposition between barium chloride and any other soluble hydroxyfluoberyllate at a low temperature. The white precipitate formed was washed with water and alcohol, and was finally dried in a desiccator. (Found : Ba, 62.35 ; F, 25.86. $BaBeF_3OH$ requires Ba, 62.33 ; F, 25.06 per cent).

This compound is almost insoluble in water. If some amount of water after being thoroughly shaken with barium hydroxyfluoberyllate be treated with dilute sulphuric acid or hydrofluoric acid, the solution turns turbid. This clearly reveals that the solubility of barium hydroxyfluoberyllate is greater than those of barium sulphate and barium fluoberyllate.

In view of insolubility of both the fluoride and the hydroxyfluoberyllate of barium in water and of the possibility of co-precipitation of fluoride and hydroxyfluoberyllate, the X-ray diffraction spectra of this compound were taken. The X-ray analysis revealed that the compound was absolutely free from barium fluoride and isomorphous with barium sulphate.

Lead hydroxyfluoberyllate was prepared by mixing a saturated solution of ammonium hydroxyfluoberyllate and a concentrated solution of lead nitrate. A heavy crystalline precipitate immediately settled down. This compound was filtered under gentle suction and washed several times with cold water and then with 60% alcohol and dried. (Found : Pb, 70.85 ; F, 19.72. $PbBeF_3OH$ requires Pb, 71.41; F, 19.64 per cent).

Like the barium salt the solubility of lead hydroxyfluoberyllate is also greater than that of lead fluoberyllate.

Cerium Hydrxyfluoberyllate.—All attempts to isolate the rare-earth fluoberyllates have failed. Owing to the dissociation of BeF_4 ion the insoluble fluoride is precipitated. The thorium nitrate titration of the potassium salts has shown that in solution the free fluoride ion is appreciably less in the case of the hydroxyfluoberyllate than the fluoberyllate. The slight secondary dissociation yielding traces of fluoride ion can easily be suppressed by the addition of some amount of amyl alcohol.

The *octahydrate* was prepared by mixing a saturated solution of cerium nitrate with a saturated solution of calculated quantity of ammonium hydroxyfluoberyllate. The temperature of the solution was always kept low by dipping the beaker in a basin containing ice and salt. The solution was stirred thoroughly during the addition of

cerium nitrate. Ice-cold water was then added to this mixture and a slight turbidity appeared. This was filtered and the resulting filtrate was heated on a water-bath. Shining crystals of octahydrated cerium hydroxyfluoberyllate began to appear. These crystals were filtered, washed with water and finally with 60% alcohol. This compound is slightly deliquescent in nature. It was analysed after drying. [Found: Ce, 41.83; Be, 4.0; F, 25.09. $Ce_2(BeF_3OH)_3, 8H_2O$ requires Ce. 41.63; Be, 4.02; F, 25.39 per cent].

Lanthanum hydroxyfluoberyllate nonahydrate was prepared from lanthanum nitrate and ammonium hydroxyfluoberyllate exactly in the same way as with cerium compound. Crystals appeared after about fifteen minutes on heating the quickly filtered resulting solution.

The shining nonahydrated crystals were filtered, washed with cold water and finally with alcohol, and dried in air. [Found: La, 40.18; Be, 3.89; F, 24.83. $La_2(BeF_3OH)_3, 9H_2O$ requires La, 40.32; Be, 3.93; F, 24.88 per cent].

The compound loses water molecules on heating to a temperature of 120°.

Mercurous Hydroxyfluoberyllate (basic salt).—When a solution of mercurous nitrate is added to a saturated solution of ammonium fluoberyllate, a black precipitate is formed.

$$(NH_4)_2BeF_4 + 2HgNO_3 \longrightarrow 2NH_4NO_3 + 2HgF + BeF_2.$$

Mercurous fluoride formed is highly soluble in water and is at once hydrolysed to HF and the black oxide (thought previously to be mercurous oxide). But the X-ray diffraction study revealed no pesence of mercurous oxide (Fricke and Ackermann, *Z. anorg. Chem.*, 1933, **211**, 233). This black percipitate is a mixture of mercuric oxide and metallic mercury. As it was expected that the linkage between beryllium and the donors was stronger in the case of hydroxyfluoberyllate, and as there were lesser number of fluoride ions present in solution in this case, attempts were made to isolate mercurous hydroxyfluoberyllate.

To a cold saturated solution of mercurous nitrate a few drops of amyl alcohol were added to suppress the secondary dissociation. To this was added a cold concentrated solution of ammonium hydroxyfluoberyllate. The solution was stirred by a glass rod when a white precipitate was formed. This was filtered quickly, washed with 80% alcohol, and analysed after drying. (Found: Hg, 84.23; F, 7.72. $HgBeF_2OH, Hg_2O, H_2O$ requires Hg, 83.73; F, 7.93 per cent).

It is to be noted that the pure mercurous sulphate can only be prepared from solution when excess of acid is present. In the absence of execss of acid basic salt of the formula Hg_2SO_4, Hg_2O, H_2O is formed.

The author acknowledges with pleasure his deep indebtedness to Prof. N. N. Ray, D. Sc. of the Presidency College and Prof. P. B. Sarkar, Dr. es. Sc. of the University College of Science for their constant patronage and for the laboratory facilities during the progress of the work. He is also indebted to Prof. P. Rây, MA., F.N.I. of the Indian Association for the Cultivation of Science for his kind interest in this investigation.

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IONIC EQUILIBRIA IN SOLUTION. PART V. LEAD LACTATE AND MONOCHLOROACETATE IN AQUEOUS SOLUTION

By Radha Charan Mohanty and S. Aditya

The solubility of lead iodate in sodium monochloroacetate and sodium lactate solution has been determined. From the solubility data the constants for the equilibria of PbA_2 (where A stands for monochloroacetate or lactate ions) in solution have been calculated.

In continuation of our earlier studies, the solubility of lead iodate in sodium monochloroacetate and sodium lactate solutions was determined with a view to having an insight into the nature of lead monochloroacetate and lead lactate in solution.

Experimental

Lead iodate was prepared by the method followed by La Mer and Goldman (*J. Amer Chem. Soc.*, 1930, **52**, 2791).

The stock solution of sodium monochloroacetate having p_H 4.82 was prepared by mixing equivalent amounts of monochloroacetic acid and caustic soda and then making up the volume. A stock solution of sodium lactate was similarly prepared by mixing equivalent amounts of lactic acid and caustic soda. With an excess of lactic acid, the ratio of salt to acid was kept equal to 100 to 1.

The solubility of lead iodate in sodium monochloroacetate and sodium lactate was determined in the same way as in the case of sodium propionate solution (this *issue*, p. 234). The results are shown in Tables I and II.

Table I

Solubility of lead iodate in sodium monochloroacetate solution.

Conc. of salt.	log s_o in KNO_3.	log s in Na monochloroacetate.	log s_o^3/s^2.	log $(s-s_o^3/s^2)$.	log $f_{Pb^{2+}}$.	$K_2\times10^2$.	$K_1\times10^2$.
0.01 *M*	$\bar{5}.8175$	$\bar{5}.8543$	$\bar{5}.7440$	$\bar{5}.2051$	$\bar{1}.8325$	2.35	6.70
0.02	$\bar{5}.8500$	$\bar{5}.9018$	$\bar{5}.7464$	$\bar{5}.3799$	$\bar{1}.7482$	2.60	9.86
0.04	$\bar{5}.8900$	$\bar{5}.9734$	$\bar{5}.7231$	$\bar{5}.6146$	$\bar{1}.6532$	2.31	9.20
0.06	$\bar{5}.9200$	$\bar{4}.0107$	$\bar{5}.7386$	$\bar{5}.7614$	$\bar{1}.5798$	2.16	10.20
0.08	$\bar{5}.9500$	$\bar{4}.1165$	$\bar{5}.6170$	$\bar{5}.9513$	$\bar{1}.5441$	1.30	3.70
0.10	$\bar{5}.9717$	$\bar{4}.1855$	$\bar{5}.5441$	$\bar{4}.0730$	$\bar{1}.4983$	0.93	2.68
0.12	$\bar{4}.0017$	$\bar{4}.2062$	$\bar{5}.5926$	$\bar{4}.0852$	$\bar{1}.4472$	1.08	3.85
0.20	$\bar{4}.0835$	$\bar{4}.3232$	$\bar{5}.6051$	$\bar{4}.2311$	$\bar{1}.3222$	0.99	5.11

Extrapolated value of $K_2=3\times10^{-2}$. Mean value of $K_1=7.310\times^{-2}$.

TABLE II

Solubility of lead iodate in sodium lactate.
(Salt : acid = 100 : 1).

Conc of salt.	log s_o in KNO_3.	log s in Na lactate.	log s_o^3/s^2.	log $(s-s_o^3/s^2)$.	log $f_{Pb^{2+}}$.	$K_2 \times 10^3$.	$K_1 \times 10^2$.
0.01 *M*	$\bar{5}.8175$	$\bar{5}.9733$	$\bar{5}.5059$	$\bar{5}.7923$	$\bar{1}.8325$	3.52	5.88
0.02	$\bar{5}.8500$	$\bar{4}.0958$	$\bar{5}.3583$	$\bar{4}.0076$	$\bar{1}.7482$	2.51	2.50
0.04	$\bar{5}.8900$	$\bar{4}.2191$	$\bar{5}.2316$	$\bar{4}.1516$	$\bar{1}.6582$	2.16	2.95
0.06	$\bar{5}.9200$	$\bar{4}.3104$	$\bar{5}.1393$	$\bar{4}.2801$	$\bar{1}.5798$	1.65	2.72
0.08	$\bar{5}.9500$	$\bar{4}.3498$	$\bar{5}.1501$	$\bar{4}.3214$	$\bar{1}.5441$	1.89	4.40
0.10	$\bar{5}.9717$	$\bar{4}.4055$	$\bar{5}.1041$	$\bar{4}.3832$	$\bar{1}.4983$	1.66	4.10
0.12	$\bar{4}.0017$	$\bar{4}.4169$	$\bar{5}.1715$	$\bar{4}.3914$	$\bar{1}.4472$	2.02	5.57

Extrapolated value of $K_2 = 4 \times 10^{-3}$. Mean value of $K_1 = 4 \times 10^{-2}$.

The higher solubility of lead iodate in both sodium monochloracetate and sodium lactate solutions, compared to that in potassium nitrate of the same concentration, suggests complex formation which may be represented as :

$$Pb(IO_3)_2 + nA^- \rightleftharpoons PbA_n^{-n+2} + 2IO_3^-,$$

where A represents either monochloroacetate or lactate ions. Accordingly,

$$K = \frac{[Pb^{2+}]\,[A^-]^n}{[PbA_n^{-(n-2)}]}.$$

In the manner described in our previous communication (*loc. cit.*) $[Pb^{2+}]$ is known from s'^3_o/s^2, where s'_o is the solubility in absence of $[A^-]$, $[PbA_n^{-(n-2)}]$ by subtracting $[Pb^{2+}]$ from the total solubility. The values of log c are then plotted against log $[PbA_n^{-(n-2)}]$ − log $[Pb^{2+}]$, which gives a straight line in both the cases with a slope nearly equal to 0.5. This showed that two A^- ions combined with one lead ion.

Now we can represent the equilibrium stages as :

$$PbA_2 \rightleftharpoons PbA^+ + A^- \quad ; \quad PbA^+ \rightleftharpoons Pb^{2+} + A^-$$

So that $K_2 = \dfrac{(Pb^{2+})\,(A^-)}{(PbA^+)}$ and $K_1 = \dfrac{(PbA^+)\,(A^-)}{(PbA_2)}$.

The two equilibrium constants for both the cases have been calculated by the method of approximation. In the calculation of K_2, it is assumed that in solution only one A^- acts with Pb^{2+} ion. Then as in the case of lead iodate in sodium propionate (see Part IV, *loc.cit.*), we have $[Pb^{2+}] = s_o^3/s^2$ and $[PbA^+] = s - s_o^3/s^2$, where s is the solubility of lead iodate in sodium monochloroacetate or lactate solution and s_o, that in potassium

nitrate solution of the same concentration. Thus, if the activity coefficient of the same valence type ion is taken to be the same in solution having the same ionic strength, we have,

$$K_2 = \frac{[s_2^3/s^2]\,[\mathrm{NaA}]}{[s - s_0^3/s^2]}\; f_{Pb^{2+}}.$$

The values of K_2 for monochloroacetate are shown in column 7 of Table I and those for lactate in column 7 of Table II.

The concentration of A^- has been taken to be equal to the concentration of the salt, and the ionic strength of the solution to be due to the presence of sodium monochloroacetate or lactate only neglecting that due to lead iodate. It is observed that, as expected, K_2 decreases as the concentration of sodium monochloroacetate or lactate increases. The extrapolated value of K_2 at zero ionic strength for lead monochloroacetate is 3×10^{-2}, and that for lead lactate is 4×10^{-2}. Taking these values of K_2, K_1 has been calculated.

Considering two-stage equilibria and making calculations in the same manner as has been done in the case of lead propionate (*loc.cit.*), K_1 has been calculated for both lead monochloroacetate and lead lactate. The results are recorded in column 8 of Tables I and II respectively.

The strengths of the acids, lead salts of which have been studied so far are in the order: monochloroacetic acid > lactic acid > acetic acid > propionic acid. When we compare the equilibrium constants, K_2, for the different lead salts, *i.e.*, $PbA^+ \rightleftarrows Pb^{2+} + A^-$, they also stand in the same order. The weaker the acid, the less dissociated its lead salt is. A similar behaviour has been reported in the case of carboxylates (Lloyds *et al.*, *J. Chem. Soc.*, 1951, 1786).

The authors wish to thank Dr. B. Prasad for his interest in the work.

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A NOTE ON PHOTO-OXIDATION OF DYES IN PRESENCE OF HYDROGEN PEROXIDE

By C. M. Desai and B. K. Vaidya

This investigation records the oxidation of dyes with simultaneous peroxide decomposition in sunlight. One of the thermal and photo-oxidation products of triphenylmethane dyes in presence of peroxide was found to be a ketone (cf. this *Journal*, 1954, **31**, 261).

Four different sets of solutions (25 c.c.) containing about 200 to 400 × $10^{-6}M$ of hydrogen peroxide (Merck) and 0.25 to 2.0 × $10^{-6}M$ of different dyes, viz. B. G., M. G., C. V., Rosaniline, picric acid, Naphthol yellow, Chrysoidine and aminoazobenzene, were exposed to sunlight (35°-37°) on clear days in January to March in pyrex flasks covered with cellophane paper. The flasks were removed at intervals and the colour fading was measured in a Leitz colorimeter by comparison with the corresponding

Fig. 1

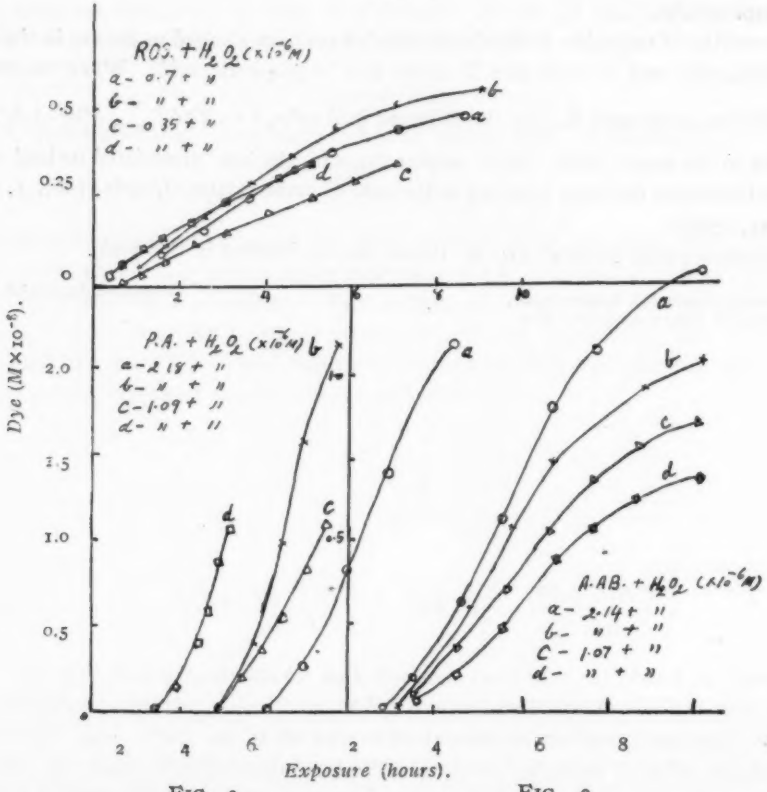

Fig. 3 Fig. 2

mixtures kept in the dark ; the peroxide was estimated by iodimetric method. The thermal reaction was distinguished from the photochemical one by means of parallel dye and peroxide estimations in another set of mixtures, placed in the sun, but wrapped with black paper. The thermal reaction for dyes was found to be negligible, but that for the peroxide was considerable, and so due allowance was made for it. The typical results of photodecomposition rate for some of the dye-peroxide mixtures are shown in Figs. 1-3.

The fading rate of dyes is initially slow, then increases and finally decreases in all cases. Hydrogen peroxide accelerates the normal photo-oxidation by about 5 to 10 times. Its decomposition rate is, however, greatly inhibited by various dyes. The relative inhibition power may be evaluated from the kinetic point of view. The peroxide decomposition (D) is directly proportional to the initial peroxide concentration (c), also to the exposure time (t) and inversely to initial amount (A) of the dye. Thus

$$D = kct/A \text{ or } k = DA/ct.$$

The constant k would be then inversely proportional to the inhibition power of the dye. The value of the constant, thus calculated for the four dye-peroxide mixtures of each of the dyes, was found to be nearly the same within limits of experimental error, the exposure time t corresponding to one half of the colour change when the process may be considered in a fairly steady state. These values ($k \times 10^{-10}$) are: B.G. 28 ; M.G. 25 ; C.V. 24 ; Ros. 16 ; Chrys. 21 ; Amino 51 ; N.Y. 66 ; P.A. 104.

The inhibition power is in the order : basic dyes and Chrysoidine > aminoazobenzene > N.Y. > picric acid. The observation that the basic dyes inhibit the photochange to a greater extent than the acid dyes, is in accordance with the results of Jen and Alyea (*J. Amer. Chem. Soc.*, 1933, **55**, 575). There is some evidence of induction period in fading of many dyes and also peroxide decomposition in initial stages. The initial slow periods seem to be too large to be accounted for by reduced light intensity, which has been calculated to be not more than 10 to 12%. Further, there seems to be a definite relation between the concentration of the dye-peroxide mixture and induction period, particularly with picric acid. For $1 \times 10^{-6}M$ of the dye concentration, the peroxide concentrations are nearly 100 : 200 : 200 : 400 ($\times 10^{-6}M$) and the corresponding induction periods are 4 : 3 : 3 : 1.6 (hours). With other dyes also, there seems to be dependence of induction period on the concentration of the dye-peroxide mixture.

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Surat.

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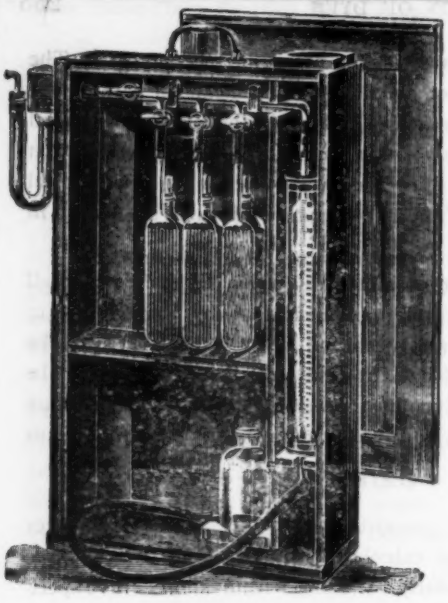

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[Jour. Indian Chem. Soc., Vol. 32, No. 5, 1955]

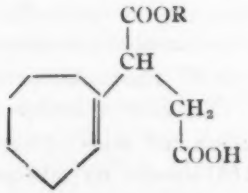
AZULENES AND RELATED SUBSTANCES. PART VI. Δ^9-OCTAHYDRO-1-OXOAZULENE AND Δ^9-OCTAHYDRO-1-OXO-3-CARBOMETHOXYAZULENE

By Sukh Dev

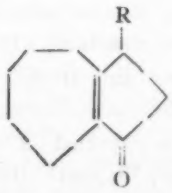
Polyphosphoric acid* has been shown to be an effective and superior reagent for the ring-closure of half-esters derived from the Stobbe condensation of succinic esters with alicyclic ketones.

The dicarboxylic acid, obtained by previous workers by the hydrolysis of the half-ester from suberone, has been shown to be a mixture of isomers, structures to which have been assigned.

In Part V of this series of communications (this *Journal*, 1954, **31**, 1) an improved procedure for the preparation of Δ^9-octahydro-4-oxoazulene was reported. The isomeric ketone, Δ^9-octahydro-1-oxoazulene (III) is an equally important intermediate in the chemistry of azulenes. Its first synthesis was achieved by Plattner and Büchi (*Helv. Chim. Acta*, 1946, **29**, 1608; Cook, Philip and Somervill, *J. Chem. Soc.*, 1948, 164) by the application of the Stobbe condensation-ring-closure procedure† to *cyclo*heptanone. Recently other routes to this ketone have been successfully explored (Braude and Forbes, *ibid.*, 1953, 2208; Islam and Raphael, *ibid.*, 1953, 2247). The overall yields of this ketone (based on suberone) by these methods are rather small (20-30%). Of these syntheses, the one utilising the Stobbe condensation in its sequence is the simplest and has the outstanding feature that the intermediate keto-ester (II) furnishes a route to azulenes carrying functional groups. Since we are also interested in the preparation of the azulene-aldehyde (IV), which can possibly lead to interesting fulvenes of the type (V), a detailed investigation in the synthesis of the keto-ester (II) and the ketone (III) has been carried out.



[Ia: R = Et; Ib: R = Me]

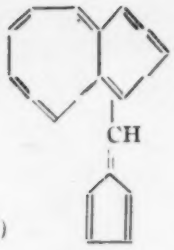


[IIa: R = CO_2Me; IIb: R = CO_2H; III: R = H]

* A preliminary report appeared in *Chem. Ind.*, 1954, 1071.

† An improved procedure (42.5% yield of crude ketone) has been very recently described by Kovats, Fürst and Günthard (*Helv. Chim Acta*, 1954, **37**, 534); also cf. Günthard, Suess, Marti and Plattner (*ibid.*, 1951, **34**, 959).

(IV)

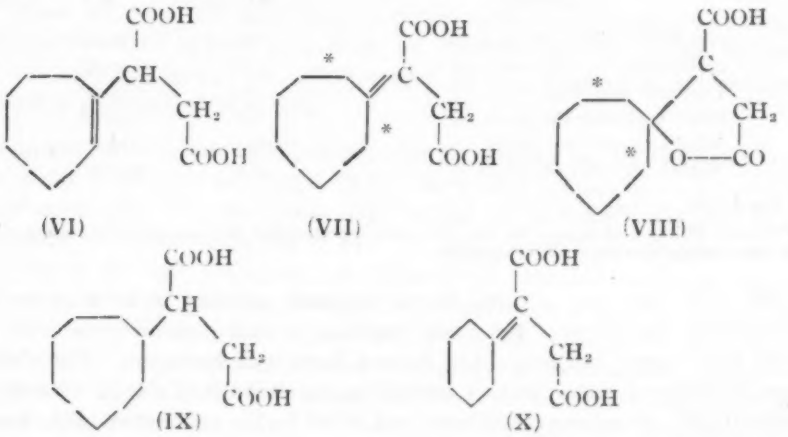


(V)

*Stobbe Condensation of cyclo*Heptanone

The half-ester (Ia) was prepared essentially by the method of Plattner and Büchi (*loc. cit.*), except that the reaction mixture, before refluxing, was set aside at room temperature for 24 hours and then heated for another 2 hours; this procedure, however, gave a material which failed to solidify. In order to check its purity, the product was hydrolysed according to the procedure of the Swiss workers, but the crude dicarboxylic acid had a much lower melting point (110°-115°); however, by using an excess of alkali an acid of melting point (155°-160°) comparable to that recorded by previous authors could be obtained. This indicates that a base-catalysed tautomerism (prototropy) is possibly involved (cf. the tautomerism of *cyclo*heptylidene-acetic acid, Hugh, Kon and Mitchell, *J. Chem. Soc.*, 1929, 1435) and the dicarboxylic acid may, in fact, be a mixture of the $\alpha\beta$- and $\beta\gamma$-unsaturated acids. This was confirmed by the fractional crystallisation of the crude acid mixture, when two homogeneous acids (A, m.p. 118-19°; B, m.p. 185-87°) could be separated. These have been assigned the structures (VI) and (VII) respectively, in view of their chemical and physical properties. Both these acids could be converted into the paraconic acid (VIII) (cf. Cook, *et al.*, *loc. cit.*) on treatment with hydrochloric acid in acetic acid. The acid (A) could be easily reduced catalytically to the corresponding succinic acid (IX); the acid (B) proved resistant. On ozonolysis, the compound (B) yielded *cyclo*heptanone, whereas the other isomer failed to give this ketone under similar conditions. In agreement with its structure (VII), the compound (B) absorbed light (λ_{max}^{EtOH}, 222; log ϵ, 3.84; cf. Plattner and Büchi, *loc. cit.*). The molar extinction coefficient is rather low; however, the related compound, (X), gave a similar value; (λ_{max}^{EtOH}, 216; log ϵ, 3.12) in the region expected of $\alpha\beta$-unsaturated acids (Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564); the acid (A) showed no maximum in the region. This clarification of the structure of the 'acid' brings the case of the acid-ester derived from *cyclo*heptanone in line with that of the corresponding *cyclo*hexanone analogue (Johnson, *et al.*, *ibid.*, 1948, **70**, 3021). Like the *cyclo*hexylidene-succinic acid (X), the acid (VII) also melts with decomposition, and this has been found out to be due to the anhydride formation. Plattner and Büchi ascribe the structure (Ia) to the crystalline half-ethyl ester on the basis that it does not absorb in the 220 mμ region; this structure has been further confirmed by its hydrolysis under mild condition to the

dicarboxylic acid (VI). Both the acids (VI and VII) are fairly resistant to interconversion on refluxing with aqueous alkali, and it appears that the prototropic shift takes place prior to the hydrolysis of the half-ester.



(VI) (VII) (VIII)

(IX) (X)

Cyclisation of the Half-ester

The crystalline dicarboxylic acid, (VII), was chosen for testing possible reagents for its cyclisation to the acid (IIb), which under the experimental conditions was expected to yield the required unsaturated ketone (III). The acetic anhydride-zinc chloride method (Bachmann and Dreiding, *J. Org. Chem.*, 1948, **13**, 324) gave only a 5% conversion. Acetic anhydride containing a trace of perchloric acid gave a similar result, while the acetic anhydride-sulphuric acid method (Kuhn and Schinz, *Helv. Chim. Acta*, 1953, **36**, 161) failed completely. Our attention was next directed to a solution of P_2O_5 in syrupy phosphoric acid (polyphosphoric acid, PPA). In recent years, this reagent has proved of considerable value in the intramolecular acylation of aryl-aliphatic acids (Koebner and Robinson, *J. Chem. Soc.*, 1938, 1995; Bachmann and Horton, *J. Amer. Chem. Soc.*, 1947, **69**, 58; Snyder and Werber, *ibid.*, 1950, **72**, 2962, 2965; Gilmore and Horton, *ibid.*, 1951, **73**, 1411; Horning and Walker, *ibid.*, 1952, **74**, 5147; Koo, *ibid.*, 1953, **75**, 720; Sukh Dev, this *Journal*, 1953, **30**, 789); however, there has been no attempt to use it for the ring-closure of purely aliphatic or alicyclic equivalents (cf. Burnop *et al.*, *J. Chem. Soc.*, 1940, 728). The dicarboxylic acid, under consideration, readily underwent cyclisation to yield the desired ketone in 42% yield. Various other compounds were then cyclised to arrive at the most convenient starting material for the preparation of *cyclo*hepteno-*cyclo*pentanone (III). The results are recorded in Table I. It should be noted that the higher melting acid (VII) furnishes a lesser yield of the ketone, and this may be taken as another proof for the correct assignment of the structures to the two isomeric dicarboxylic acids, as it is well known that the endocyclic double bond undergoes ring-closure with greater ease (cf. Villani, King and Papa, *J. Org. Chem.*, 1953, **18**, 1578).

TABLE I*

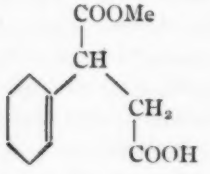
Cyclisations with polyphosphoric acid.

No.	Compound.	Wt. of DNP.	M.P.	Ketone (%).
1	*cyclo*Heptenylsuccinic acid (VI)	700 mg.	216-19°	42.4
2	*cyclo*Heptylidene-succinic acid (VII)	300	222-26°	18.0
3	Paraconic acid (VIII)**	480	219-22°	29.0
4	Ethyl acid-ester (Ia, pure)	700	215-18°	42.4
5	Ethyl acid-ester (Ia, crude)	850	218-20°	51.5
6	Methyl acid-ester (Ib crude)	850	217-20°	51.5

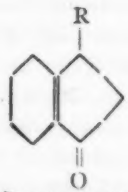
* For details, see Experimental.

** Cook, Philip and Somerville (*loc cit.*) have reported that this lactonic acid could not be cyclised by the acetic anhydride-zinc chloride method.

The next step was a study of the different variables to arrive at the optimum experimental conditions. For this purpose, several experiments were carried out on the methyl half-ester (XI) derived from *cyclo*hexanone. The yields of the ketone, as obtained under various conditions, are shown in Table II. Based on these considerations, procedures have been worked out for the preparation of the unsaturated keto-ester or the ketone derived from the half-ester (Ia or XI). The conditions had to be modified still further in order to avoid the use of large quantities of PPA. One way out was found in the use of PPA containing a higher concentration of phosphorus pentoxide; with this reagent a smaller time of reaction sufficed to give comparable yields of the desired compounds.



(XI)



[XII, R = CO_2Me; XIII, R = H]

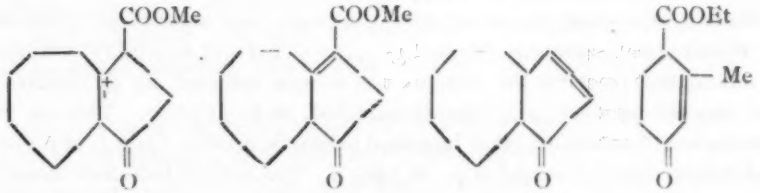
TABLE II

Cyclisation of (XI): *Effect of temp. and time.*

No.	Time.	Ketone (%) (2:4-DNP method).	No.	Time.	Ketone (%). (2:4-DNP method)
	Temp. = 97° (boiling water-bath).			Temp. = 85° 90°.	
1	1 hr.	25.3	1	6 hrs.	44.3
2	2	38.0	2	12	53.7
3	3	50.6	3	15	55.0
4	4	50.6	1	Temp. = 70°-75°.	19.0
5	6	44.3	2	6	22.1
6	2½	44.3		12	
7	3½	65.0	1	Room temp. (22-24°). 20 days	9.5

Polyphosphoric acid, thus, appears to be a useful reagent for the intramolecular acylation of suitable compounds in the alicyclic or aliphatic series. It is the reagent of choice for the preparation of *cyclo*hepteno-*cyclo*pentanone. Anderson and Tazuma (*J. Amer. Chem. Soc.*, 1953, **75**, 4979) have recently synthesised-Δ^9-octahydro-1-oxo-3-carbomethoxyazulene (IIa) in 7.9% yield from the methyl half-ester (Ib) by the zinc chloride-acetic anhydride procedure ; PPA method, on the other hand, has furnished this compound in an overall yield of 60%.

The expected intermediate (XIV) during the ring-closure of the half-ester can eliminate a proton to afford either (IIa) or (XV). Both these compounds on hydrolysis-decarboxylation can give rise to the ketone (III), though the $\alpha\beta$-unsaturated ester (XV) can also produce the isomeric ketone (XVI). In order to settle the structure of the cyclisation product, the light absorption properties of the keto-ester and its derivatives have been examined. The keto-ester displays its maximum at 238 mμ (log ϵ, 4.14) ; the position of maximum absorption is almost the same as that of the ketone (III) ($\lambda_{max.}$ 240 mμ ; log ϵ, 4.12). An $\alpha\beta\beta$-trisubstituted *cyclo*pentenone is expected to display its principal band at 236 ± 5 mμ (Frank, Armstrong, Kwiatek and Price, *ibid.*, 1948, **70**, 1379 ; French and Wiley, *ibid.*, 1949, **71**, 3702). The formulation of the keto-ester as (IIa) is thus supported on spectral grounds. It may be pointed out that the disposition of the functional groups in this compound is the same as in the Hagemann's ester (XVII);



(XIV) (XV) (XVI) (XVII)

however, the latter compound shows (λ_{max}^{MeOH}, 230; ϵ, 12900; Acheson and Robinson, *J. Chem. Soc.*, 1952, 1130) a small hypsochromic shift with respect to the maximum of the corresponding ketone (λ_{max}^{EtOH}, 235 ; ϵ, 12930 ; Evans and Gillam, *ibid.*, 1941, 816). The semicarbazone derived from the keto-ester (IIa) showed its intense band at 270 mμ (log ϵ, 4.32) *i.e.*, within the range where the semicarbazones derived from $\alpha\beta$-unsaturated carbonyl compounds are expected to absorb (Gillam and Evans, *ibid.*, 1943, 565). However, the case of the corresponding 2 : 4-dinitrophenylhydrazone is a little anomalous ; its maximum at 389 mμ (log ϵ, 4.43) is at an appreciably lower wave-length than the position of the principal absorption band for the 2 : 4-dinitrophenylhydrazone of the ketone (III) ($\lambda_{max}^{chloroform}$, 396 m$\mu$; ϵ, 29500 ; Braude and Forbes, *ibid.*, 1953, 2208) ; this is also reflected in the colour of the 2 : 4-dinitrophenylhydrazones, the one derived from the keto-ester is orange, whereas the derivative from the ketone (III) has a dark red colour (cf. Mathieson, *ibid.*, 1953, 3251).

EXPERIMENTAL*

Suberone was prepared according to the procedure of Kohler *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 1059 ; cf. Blicke, Doorenbos and Cox, *ibid.*, 1952, **74**, 2924). The product had b.p. 173-74°/684 mm. ; n_D^{24}, 1.4600.

Stobbe Condensation of Suberone with Dimethyl Succinate. (cf. Anderson and Tazuma, *loc. cit.*).—A mixture of suberone (22.5 g, 0.2*M*) and dimethyl succinate (58.4 g., 0.4*M*) was added in one lot to a cold solution of potassium (8.6 g., 0.22 g. atom) in *tert.*-butyl alcohol (180 c.c.). The yellow reaction mixture was left overnight (15 hours) at room temperature (28°) and then refluxed for 2 hours (nitrogen atmosphere for all operations). The dark reaction mixture was chilled and acidified with cooling to p_H 2 with dilute HCl (1 : 1 ; *ca.* 54 c.c.). The colour changed from dark red to light orange through light yellow. The solvent was next fractionated off (1 ft. Vigreux column) under vacuum (water-pump) from a water-bath. The residue was cooled, diluted with water (100 c.c.) and dilute ammonium hydroxide (10% ; *ca.* 75 c.c.) added till ammoniacal. The neutral material was extracted with ether (50 c.c. × 3) ; this was washed with dilute ammonium hydroxide (25 c.c. × 2) and then with water (50 c.c.). The combined aqueous alkaline solution was extracted back once with ether and acidified (p_H 2) with dilute hydrochloric acid (1 : 1 ; *ca.* 100 c.c.) with cooling in an ice-bath. The liberated half-ester was taken up in ether (50 c.c. × 3), washed with brine (50 c.c. × 3) and dried (Na_2SO_4). After complete removal of the solvent, the required compound was obtained as a red syrup (49.3 g.). This was cyclised directly.

When the corresponding amount of ethyl succinate was substituted in the above preparation, the ethyl half-ester was obtained (50 g.) which failed to solidify. However, when after mixing the reactants the mixture was at once refluxed for 45 minutes and then worked up, the product (40 g.) slowly solidified (m.p. 55°-60°). This on three recrystallisations from petroleum ether furnished prismatic needles (24 g.), m.p. 70-71° (Plattner and Büchi, *loc. cit.*, record m.p. 68.5-69°). The methyl half-ester could not be obtained crystalline under these conditions.

Hydrolysis of the Ethyl Half-ester.— A solution of the ethyl half-ester (syrup, 5 g.) in aqueous sodium hydroxide (5 g. in 50 c.c. of water) was heated on the steam-bath for 6 hours and then worked up to furnish an acid product (3.2 g.), m.p. 155°-160°.

However, when the half-ester (40 g.) was hydrolysed with lesser amount of sodium hydroxide (25 g. in 250 c.c. of water) a product of m.p. 110°-115° was obtained ; yield 25 g. This on recrystallisation from acetic acid (50 c.c.) containing water (50 c.c.) yielded a material (B, 8 g.) of m.p. 185-87° (with efferv.). The mother-liquor was diluted with water (1000 c.c.) and the clear solution allowed to stand overnight for crystallisation ; a second product (A, 14 g.) of m.p. 115-16° separated.

The *acid* (*B*) was recrystallised from dilute acetic acid (1 : 1) to furnish white needles, m.p. 185-87° with gas evolution ; yield 6.7 g. (Found : C, 62.27 ; H, 7.72 ; neut. equiv., 107. $C_{11}H_{16}O_4$ requires C, 62.26 ; H, 7.54 per cent. Neut. equiv., 106). Light absorption : λ_{max}^{EtOH}, 222 mμ ; log ε, 3.84.

All melting and boiling points are uncorrected. Petroleum ether refers to the fraction of b.p. 40°-60°. Spectra were taken on Beckman DU spectrophotometer.

An one gram sample was decomposed at its melting point in a current of nitrogen, the evolved gases were bubbled through aqueous barium hydroxide. No CO_2 was evolved and the decomposition residue on treatment with water regenerated the original acid quantitatively. When the acid (500 mg.) was heated with aqueous sodium hydroxide (500 mg. in 5 c.c. of water) for 6 hours on the steam-bath and then worked up, it was essentially recovered unchanged (400 mg., m.p. 184-85°). Its sodium salt is sparingly soluble in water.

On two recrystallisations from hot water (250 c.c.) the *acid* (A) gave white, soft needles, m.p. 118-19°, yield 9 g. (Found: C, 62.24; H, 7.6; neut. equiv., 106. $C_{11}H_{16}O_4$ requires C, 62.26; H, 7.54 per cent. Neut. equiv., 106). On a similar treatment (*vide supra*) with aqueous sodium hydroxide a product (400 mg.) with m.p. 114-17° was recovered. Its sodium salt is easily soluble in water. This was the only acid isolated when the crystalline half-ethyl ester (Ia; 1 g.) was hydrolysed at room temperature with $Ba(OH)_2$ (1 g. in 50 c.c. H_2O).

Lactonisation of the Acids.— A mixture of the acid (2.12 g., 0.01 *M*), acetic acid 10 c.c.) and HCl (C.P., 50 c.c.) was gently refluxed for 4 hours. After leaving overnight the product crystallised out; this was well-chilled for several hours and then the compound collected on a filter, washed with water and dried. Both isomers yielded 1.2 g. of a material, m.p. 185°; two recrystallisations from acetic acid (10 c.c.) containing water (30 c.c.) afforded white prisms, m.p. 187-89° (with efferv.), yield 0.7 g.; mixed m.p. with the isomer (B) was 160-64° with previous shrinking. (Found: C, 62.8; H, 7.3. $C_{11}H_{16}O_4$ requires C, 62.26; H, 7.54 per cent). Cook, Philip and Somerville (*loc. cit.*) separated a lactonic acid (m.p. 184-86°) from the acidic portion of the cyclisation products of the half-ester. This must be identical with the paraconic acid (VIII) described now.

Ozonolysis of the Acids.—The *acid* (B) (212 mg., 0.001*M*) was dissolved in warm acetic acid (40 c.c.), diluted with water (10 c.c.) and ozonised at 0° with ozonised oxygen till ozone passed freely (KI-boric acid test; 15 mins.). To the ozonised solution zinc dust (1 g.) was added and after leaving at room temperature (20°) for one hour, it was diluted with water (50 c.c.) and distilled to collect the distillate (*ca.* 80 c.c.). To this a solution of the 2:4-dinitrophenylhydrazine (200 mg. in 2 c.c. of concentrated sulphuric acid and diluted with 2 c.c. of water and then 10 c.c. of ethanol added) was added. The precipitated derivative was collected after 12 hours and washed with dilute alcohol (1:1; 20 c.c.) and dried; yield 120 mg. (41.7%) of a material with m.p. 130-34°. This after three crystallisations from alcohol furnished yellow leaflets (70 mg.), m.p. 144-45°; mixed m.p. with an authentic sample (m.p. 147-48°) of suberone 2:4-dinitrophenylhydrazone was 145-46°.

The isomeric acid (m.p. 118-19°) under these conditions gave only a negligible amount (*ca.* 5 mg.) of the precipitate; this was not investigated further.

When an equivalent amount of suberone (0.112 mg., 0.001 *M*) was dissolved in acetic acid (40 c.c.) containing water (10 c.c.) and treated with zinc dust as above, the yield of the precipitated 2:4-dinitrophenylhydrazone (m.p. 137-40°) was 220 mg. (75.8%). This after three crystallisations from alcohol gave yellow leaflets (170 mg.), m.p. 147-48°.

cyclo*Heptylsuccinic Acid* (IX).—The lower-melting isomer (A, 400 mg.) was hydrogenated (room temp.) over pre-reduced platinum oxide catalyst (20 mg.) in acetic acid (25 c. c.); 104% of the theoretical amount of hydrogen was absorbed in 15 minutes, when the reduction came to a close. The catalyst and the solvent (water-bath/water-pump) were removed and the residue crystallised from water (20 c.c.) at 0-5°. The *cyclo*heptylsuccinic acid was obtained as colorless prisms (300 mg.), m.p. 120-22°; mixed m.p. with the starting material was 100°-105°. (Found: C, 61.65; H, 8.38. $C_{11}H_{18}O_4$ requires C, 61.68; H, 8.41 per cent). The isomeric dicarboxylic acid could not be reduced under these conditions.

Ring-closure Experiments.—Polyphosphoric acid was prepared by adding syrupy phosphoric acid (*d* 1.75, 6 c.c.) in one lot to P_2O_5 (10 g.) contained in a wide test-tube (cap. 50 c. c.); this was immediately stirred with a glass rod till homogeneous; the heat of the reaction sufficed for the almost complete dissolution of the anhydride: if any particles remained undissolved, it was heated (guard-tube) on the steam-bath till clear.

The data recorded in Table I were obtained by adding 0.005 *M* of the compound to the above polyphosphoric acid, and after mixing well (glass rod) the mixture was heated (moisture protection) on the steam-bath for 1½ hours. The cooled, dark reaction mixture was decomposed by adding in ice (20 g.). This was diluted with water to about 250 c. c. and slowly distilled till a 2,4-dinitrophenylhydrazone test was negative (*ca.* 150-200 c. c. of the distillate). To the distillate a solution of the 2:4-dinitrophenylhydrazine (1 g. in 10 c. c. of conc. H_2SO_4) in alcohol (80 c. c.) was added; the mixture was heated to boiling and then left aside as such. The precipitate was collected after 12 hours, washed with ice-cold alcohol (15 c. c.) and dried to a constant weight. The derivative on two crystallisations from glacial acetic acid furnished dark red, lustrous leaflets, m.p. 229-30°. Braude and Forbes (*loc. cit.*) give the m.p. of the 2:4-*dinitrophenylhydrazone* of Δ^9-*octahydro-1-oxoazulene* as 226°, whereas Islam and Raphael (*loc. cit.*) report m.p. 230°.

A similar study on the methyl half-ester derived from *cyclo*hexanone (*vide infra*) gave the results tabulated in Table II; the average m.p. of the precipitated 2:4-dinitrophenylhydrazone was 218-22°. Two recrystallisations from xylene gave dark red, shining leaflets, m.p. 229-30° (constant). Mathieson (*J. Chem. Soc.*, 1951, 177) records 238° (corr.) as the m.p. of the derivative from 4:5:6:7-tetrahydroindane-1-one.

Δ^9-*Octahydro-1-oxo-3-carbomethoxyazulene* (IIa).—For preparative scale cyclisation, the PPA is best prepared as follows (cf. Gilmore and Horton, *loc. cit.*): To phosphorus pentoxide (140 g.), contained in a flask equipped with a Hershberg stirrer and protected from moisture, orthophosphoric acid (85%, 60 c.c.) is added with stirring during one minute; the mixture which becomes very hot is vigorously stirred till almost all the particles of P_2O_5 have dissolved (*ca.* 15 minutes); if the stirring has not been smooth, it may be found necessary to gently warm the mixture with a micro-burner till an almost clear solution is obtained (another 10-15 minutes). The stirring is then discontinued and the PPA allowed to attain room temperature. This quantity of PPA is sufficient to cyclise (*ca.*) 0.2 mole of the material.

The crude methyl half-ester (*vide supra*) corresponding to 0.2 mole of suberone was added to the above quantity of PPA (15 c. c. of petroleum ether was used to wash in the last traces of the half-ester) and the well-mixed product heated (no stirring; silica gel guard tube) on the steam-bath for one hour with occasional mixing (mixing should be frequent in the beginning till the reaction mixture becomes homogeneous). The dark brown reaction mixture was cooled in an ice-bath and powdered ice (*ca.* 200 g.) added to this. It was diluted with water to about 800 c. c. and after dissolving in ammonium sulphate (150 g.), the keto-ester was taken up in ether (70 c. c. × 4) ; the combined extract was washed with water (50 c. c.) and then with sodium bicarbonate solution (5%; 70 c. c. × 3). The alkaline washings were extracted back with ether (70 c.c.) and after clarification with norit acidified to give an acid (1.5-2.5 g.), identified as *cyclo*heptylidene-succinic acid (initial m.p. 174-77° ; after recrystallisation from dilute acetic acid, m.p. 184-85° ; mixed m. p. with an authentic sample, 185-86°. The combined ether solution was washed with brine (70 c. c. × 2) and dried (Na_2SO_4). This was stripped off the solvent and the residue fractionated to collect three fractions: (*i*) up to 136°/0.6 mm., yield 1-1.5 g., chiefly the Δ^9-octahydro-1-oxoazulene; (*ii*) 136-137°/-0.6mm., yield 25.5 g. and (*iii*) b.p. 166°-170°/0.6 mm., 2-3 g. This on exposure to atmosphere slowly started solidifying ; hence this presumptive anhydride fraction was treated with water and the acid identified as *cyclo*heptylidene-succinic acid. The second fraction represents 61.3% yield of the desired keto-ester (based on suberone); it is a colorless, somewhat viscous liquid. An analytical sample (refractionation; central cut) had b. p. 126°/0.15mm.; n_D^{22}, 1.5150 ; n_D^{30} , 1.5110 ; λ_{max}^{EtOH}, 238 mμ; log ε, 4.14. (Found: C, 69.61 ; H, 7.57. $C_{12}H_{16}O_3$ requires C, 69.23 ; H, 7.68 per cent).

The *semicarbazone* was prepared by the pyridine method. It crystallised in white needles from a mixture of pyridine and alcohol (1:2), m.p. 231-32° (decomp.) when introduced in a bath at 220°; λ_{max}^{EtOH}, 270 mμ; log ε, 4.32. (Found : N, 16.0. $C_{13}H_{19}O_3N_3$ requires N, 15.84 per cent).

The 2 : 4-*dinitrophenylhydrazone* (HCl method) crystallised from ethanol as orange-red plates, and from a mixture of benzene and petroleum ether, as small nodules of orange-red prisms; both had m.p. 188-89° (Anderson and Tazuma, *loc. cit.*, report m.p. 185-187°) ; $\lambda_{max}^{CHCl_3}$, 389 mμ; log ε, 4.43. (Found: N, 14.1. $C_{18}H_{20}O_6N_4$ requires N, 14.4 per cent).

Δ^9-*Octahydro-1-oxoazulene* (III).—The preparation was carried out exactly as above. After decomposition of the PPA reaction mixture and diluting it with water to *ca.* 600 c. c., acetic acid (100 c. c.) was added and the whole heated on the steam-bath (reflux) for 4 hours to effect decarboxylation. This was cooled, diluted with water to a total of *ca.* one litre and after dissolving in ammonium sulphate (200 g.), extracted with ether (100 c. c. ×4). The combined ether extract was washed with brine (100 c. c.) and then extracted with saturated $NaHCO_3$ solution to remove acidic material. (On being worked up as above the alkaline washings yielded 5-6 g. of *cyclo*heptylidene-succinic acid) ; the alkaline portion was back-extracted with ether (100 c. c.); this was mixed with the main ethereal portion and washed with brine

(100 c. c. × 2) and dried (Na_2SO_4). The solvent was flashed off and the residue fractionated to furnish Δ^9-octahydro-1-oxoazulene as a colorless liquid with a strong odour, b. p. 104°/2.5 mm., yield 17 g. (56.6% based on suberone). An analytical sample had b.p. 131°/12 mm.; n_D^{30}, 1.5200 ; λ_{max}^{EtOH}, 240 mμ; log ε, 4.12; 2 : 4-dinitrophenylhydrazone, m.p. 229-30° (*vide supra*). (Braude and Forbes, *loc. cit.* give b.p. 180°/0.8 mm. n_D^{21}, 1.5237).

Methyl 4 : 5 : 6 : 7-*Tetrahydro-3-oxo-indane-1-carboxylate* (XII).— *cyclo*Hexanone was condensed with dimethyl succinate following the procedure of Mathieson (*J. Chem. Soc.*, 1953, 3251); yield of the crude half-ester was quantatitative and that of the distilled material (b. p. 153-155°/0.8 mm. n^{24}, 1.4930) was 83.3%.

The crude half-ester (≡0.2 *M* of *cyclo*hexanone) was cyclised with PPA by following the details given above for the *cyclo*heptanone analogue. The required keto-ester (XII) was obtained as a colorless liquid, b. p. 119°-122°/0.25 mm. ; n_D^{25}, 1.5060; yield 22.3 g. (57.4%) (Mathieson, *loc. cit.* gives b.p. 112°-115°/0.2 mm. ; n_D^{21}, 1.5056).

4 : 5 : 6 : 7-*Tetrahydroindan-1-one* (XIII) was prepared by closely following the details outlined above for the preparation of Δ^9-octahydro-1-oxoazulene. The yield of the desired ketone of b.p. 141°/30 mm. (n_D^{25}, 1.5225) was 47-55% (Mathieson, *J. Chem. Soc.*, 1953, 3248, reports b.p. 83.5-85°/2 mm. n_D^{18} 1.5260). Light absorption in ethanol : λ_{max} , 237; log ε, 4.11 (Braude and Coles, *ibid.*, 1952, 1430, give λ_{max} , 237; ε, 12500).

The alkaline washings gave 6-8 g. of an acid, of m.p. 171-73° ; repeated recrystallisations from dilute acetic acid (1 : 1) gave white, felted needles, m.p. 190-91° with gas evolution ; this must be the *cyclo*hexylidene-succinic acid (Mathieson, *ibid.*, 1953, 3251, gives m.p. 193°, whereas Johnson *et al.*, *loc. cit.*, report m.p. 179-180°). The identification was further confirmed by lactonisation to the corresponding paraconic acid by treatment with hydrochloric acid (for details *vide supra*) when white prisms (two crystallisations from dilute acetic acid) of m.p. 186-87.5° were obtained ; yield, 80%. (Johnson *et al.*, *loc. cit.*, cite m.p. 186-87° for the paraconic acid).

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EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART V

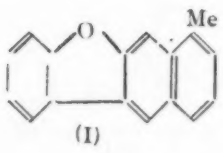
By J. N. Chatterjea

The synthesis of β-brazans from coumaran-diones and phenacyl halides has been extended. New syntheses of β-brazanquinone and a synthesis of the quinone (VIII) are reported. These syntheses involve ring-closure at the β-position of the furan ring.

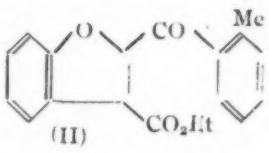
A synthesis of the seven-membered lactone (XIII) and the lactam (XV) is reported.

The experiments described in this communication were made during the course of an exploratory work on the alternative approaches to the β-brazan ring system and on the extension of the novel synthesis developed in Part III of this series (Chatterjea, this *Journal*, 1954, **31**, 101) and these are recorded collectively on account of their independent interest.

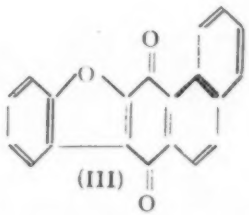
The synthesis of β-brazanquinone and the related brazans from coumaran-diones and phenacyl halides is capable of wide variation as shown by the syntheses of β-brazanquinone and its 3-methoxy, 3:8:9-trimethoxy and 3:4:8:9-tetramethoxy derivatives (Chatterjea, *loc. cit.*). As a further example, 7-methyl-β-brazan (I), which was previously synthesised from diphenylene oxide (*ibid.*, 1953, **30**, 103), has now been obtained by the new method mentioned above. The condensation of coumaran-dione with *o*-methylphenacyl bromide (Baker, *J. Chem. Soc.*, 1938, 445) in alcoholic sodium ethoxide afforded ethyl 2-*o*-toluoylcoumarone-3-carboxylate (II). This was hydrolysed and the related acid (II, H in place of Et) on cyclisation by way of the acid chloride yielded 7-methyl-β-brazanquinone.



(I)



(II)



(III)

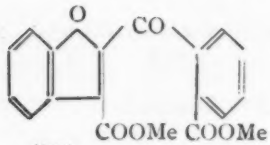
Reduction of the quinone with hydriodic acid gave the β-brazan (I), whilst catalytic reduction with Pt gave the corresponding colorless quinol which rapidly oxidised to the quinone by atmospheric oxygen.

o-Methylphenacyl bromide was prepared from *o*-methylacetophenone (Baker, *loc. cit.*). The latter was conveniently obtained from *o*-toluoyl chloride and magnesium malonic ester according to Walker and Hauser (*J. Amer. Chem. Soc.*, 1946, **68**, 1386).

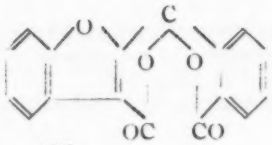
In the same way, 7:8-benzo-β-brazanquinone (III) was prepared from coumaran-dione and 1-chloroacetylnaphthalene (Widman, *Ber.*, 1918, **51**, 907).

An obvious variation of the synthesis of β-brazanqinone is by the condensation of coumaran-dione with *o*-carbomethoxyphenacyl bromide (Gabriel, *Ber.*, 1907, **40**, 73,

4227) in alcoholic sodium methoxide to give the ester (IV). Attempts to prepare the anhydro-dilactone (V) from the corresponding acid, preliminary to its conversion into β-brazanquinone (cf. Mayer, *Annalen*, 1931, **488**, 291 ; Mills and Nodder, *J. Chem. Soc.*, 1921, **119**, 2094), have not been successful. The quinone was obtained, however, albeit in poor yield, through pyrolysis of corresponding barium salt.



(IV)



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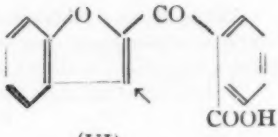
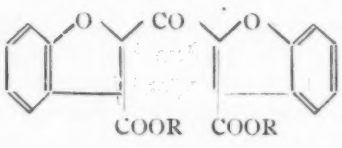


(VI)

In Part III of this series, a synthesis of the acid (VI) was described. Although this acid does not undergo cyclisation with phosphoric acid (cf. Koo, *J. Amer. Chem. Soc.*, 1953, **75**, 1891), acetic anhydride, phosphoric anhydride or by way of the acid chloride, it has now been found that this cyclisation can readily be brought about by H_2SO_4 at 100°, and thus effecting ring-closure at the β-position of the furan ring. The potential usefulness of this cyclisation * is far reaching.



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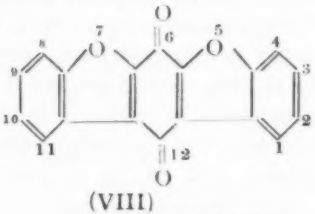

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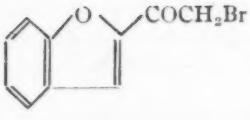

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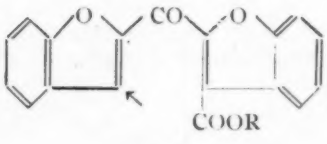
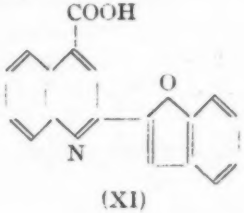


(X)



(XI)

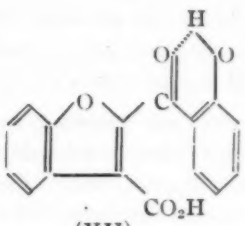
Condensation of coumaran-dione with *sym.*-dichloroacetone in alcoholic sodium ethoxide furnished the keto-ester (VII, R = Et). The corresponding acid (VII, R = H) could not again be converted into the dilactone of type (V). This acid, on pyrolysis, furnished a negligibly small quantity of an orange-red material, probably the quinone (VIII), but the major product was an acidic material of m.p. 162°. Unfortunately, the paucity of this material at our disposal did not permit an elaborate examination of its nature. A better approach to the synthesis of the quinone (VIII) was, however, achieved in the following way. Coumaran-dione on condensation with 2-bromoacetylcoumarone (IX) (Shriner and Anderson, *J. Amer. Chem. Soc.*, 1939, **61**, 2706) in the usual

* Cyclisation at the β-position of the thiophene ring is known (Mayer, *loc. cit.*) and a recent example of cyclisation at the β-position of the furan ring is provided by Treibs and Heyer (*Chem. Ber.*, 1954, **87**, 1197).

manner furnished the keto-ester (X). The corresponding acid, on cyclisation under controlled conditions, through the acid chloride, afforded the desired quinone in poor yield. Thus, another example of cyclisation at the β-position of the furan ring is provided. 2-Acetylcoumarone on the Pfitzinger synthesis with isatin gave the quinoline derivative (XI).

Condensation of coumaran-dione with *o*-methoxyphenacyl chloride provided the keto-ester (II, OMe in place of Me). This ester on boiling with HBr in acetic acid underwent hydrolysis and demethylation, furnishing the acid (XII) (cf. Baker *et al.*, *J. Chem. Soc.*, 1952, 1452). This acid cyclised to the seven-membered lactone (XIII) on treatment with acetic or propionic anhydride (cf. Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 3347; Baker *et al.*, *loc. cit.*).

2-*o*-Nitrobenzoylcoumarone-3-carboxylic acid (XIV), which was similarly prepared from coumaran-dione and *o*-nitrophenacyl bromide, yielded, on alkaline reduction with ferrous sulphate and ammonia, the corresponding amino-acid which provided the seven-membered lactam (XV) on treatment with acetic anhydride.



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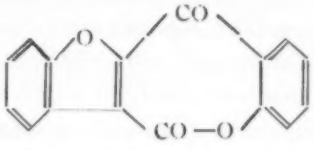

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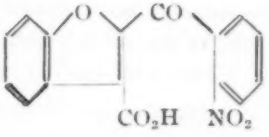

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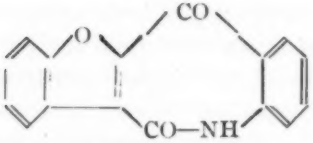
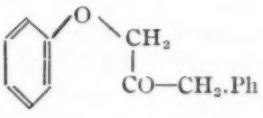
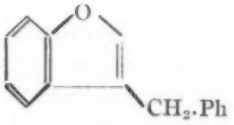


(XV)



(XVI)



(XVII)

Experiments were also carried out to extend the β-brazan synthesis from 3-benzylcoumarones (Part I, this *Journal*, 1953, **30**, 1). 3-Benzylcoumarone (XVII) itself was obtained from benzylmagnesium chloride and coumaranone, but attempts to obtain it from 1-phenyl-3-phenoxyacetone (XVI, Pfeiffer and Epler, *Chem. Abs.*, 1941, **35**, 454; cf. *Ber.*, 1929, **62**, 1249) by cyclodehydration with H_2SO_4 were unsuccessful primarily due to the formation of coumarone resins. Preliminary experiments on the Gattermann synthesis with the coumarone (XVII) so as to obtain the 2-formyl derivative, have not given encouraging results, and it is indended to study this aspect of the problem in future.

EXPERIMENTAL*

o-Methylacetophenone (cf. Walker and Hauser, *loc. cit.*).—Magnesium ethoxide was prepared by heating (with exclusion of moisture) a mixture of clean magnesium

*All m. p. 's are uncorrected.

turnings (1.3 g.), dry alcohol (1.2 c.c.) and CCl_4 (0.2 c.c.). When the reaction started a mixture of alcohol (5 c.c.), dry ether (45 c.c.) and diethyl malonate (8.8 g.) was added cautiously with stirring. The mixture was gently refluxed till all the magnesium nearly dissolved and then freshly prepared *o*-toluoyl chloride (7.8 g.) in ether (15 c.c.) was added with continued stirring, and the mixture heated further for 1 hour when the magnesium complex separated as a jelly. The reaction mixture was decomposed with dilute H_2SO_4 and the ethereal layer which contained the *o*-toluoylmalonate was taken, the solvent removed and the residue boiled for 4 hours with a mixture of acetic acid (15 c.c.), H_2SO_4 (2 c.c.) and water (10 c.c.). Then the reaction mixture was basified, the resulting oil extracted with ether, washed with water and dried (sodium sulphate). *o*-Methylacetophenone was obtained as a colorless oil, b.p. 210-12°/760 mm. (Baker, *loc. cit.*, gives b.p. 93-94°/13 mm), yield 6.5 g.

ω-Bromo-o-methylacetophenone (cf. Baker, *loc. cit.*).—A solution of the preceding ketone (4.0 g.) in $CHCl_3$ (20 c.c.) was gradually treated in cold (10°-20°) with a solution of bromine (5.0 g.) in $CHCl_3$ (15 c.c.). Decolorisation of bromine took place after a few minutes. After the addition, the chloroform solution was washed with sodium carbonate solution, dried with sodium sulphate and the lachrymatory oil, obtained after removal of the solvent, distilled at 132-34°/7 mm. (lit., b.p. 113.5°/1.7 mm.) ; yield, 5.1 g. (Found : C, 50.6 ; H, 4.5. Calc. for C_9H_9OBr : C, 50.7 ; H, 4.3 per cent).

7-Methyl-β-brazan.—Ethyl 2-o-*toluoylcoumarone-3-carboxylate* was prepared from the above bromo-ketone (2.2 g.) and coumaran-dione (1.48 g.) when condensed in alcoholic sodium ethoxide from sodium (0.23 g.) and dry alcohol (15 c.c.) for 1 hour. This was obtained from alcohol in colorless plates (1.8 g.), m.p. 96°, developing intense yellow coloration with H_2SO_4. (Found : C, 73.9 ; H, 5.2. $C_{19}H_{16}O_4$ requires C, 74.0; H, 5.2 per cent). On hydrolysis with alcoholic sodium hydroxide in the usual way, the ester (1.7 g.) furnished the related *acid* (1.5 g.), crystallising from 80% acetic acid in cream-coloured plates, m.p. 130°. (Found : C, 72.5; H, 4.5. $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3 per cent).

The acid (0.7 g.) was converted into the acid chloride by keeping overnight with thionyl chloride (6 c.c.), followed by its careful removal in vacuum. The gummy acid chloride was dissolved in dry CS_2 (10 c.c.) and treated in cold with $AlCl_3$ (2.0 g.). After 6 hours, the mixture was decomposed with ice and HCl, volatile materials removed by steam distillation, and the crystalline residue washed with dilute alkali. On crystallisation from acetic acid, *7-methyl-β-brazanquinone* was obtained in yellow needles, m.p. 222°. (Found: C, 78.0 ; H, 3.8. $C_{17}H_{10}O_3$ requires C, 77.9 ; H, 3.8 per cent).

The above quinone was also obtained by dissolving 7-methyl-β-brazan (0.1 g.) (Part II, this *Journal*, 1953, **30**, 103) in acetic acid (3 c.c.) and treating at the boiling point with a solution of chromic acid (0.35 g.) in water (5 c.c.). After the exothermic reaction was over, the mixture was boiled for 30 seconds and cooled when the quinone crystallised from acetic acid in yellow needles, m.p. and mixed m.p. 222°. The compound dissolves in H_2SO_4 with a crimson colour. Reduction of the quinone (0.2 g.) with boiling HI (10 c.c.) for 1½ hours gave 7-methyl-β-brazan (0.12 g.), crystallising

from alcohol in colorless needles, m.p. and mixed m.p. 117°. (Found: C, 87.6; H, 5.2. Calc. for $C_{17}H_{12}O$: C, 87.9; H, 5.2 per cent).

Reductive acetylation of the quinone gave 6:11-*diacetoxy-7-methyl-β-brazan*, crystallising from acetic acid in colorless needles, m.p. 270-72° (with darkening). (Found: C, 72.3; H, 4.9. $C_{21}H_{16}O_5$ requires C, 72.4; H, 4.6 per cent).

Catalytic Reduction of 7Methyl-β-brazanquinone.—The quinone (0.2 g.) was suspended in alcohol (20 c.c.) and shaken in an atmosphere of hydrogen in the presence of Adams's catalyst (0.05 g.). After a short induction period, the absorption of hydrogen was quick; the suspended material rapidly went into solution developing an intense violet fluorescence, and colorless prisms of the quinone were soon deposited. Attempts to isolate the material were unsuccessful due to the quick oxidation by atmospheric oxygen to the quinone with concomitant disappearance of the fluorescence.

7:8 *Benzo-β-brazanquinone.*—*Ethyl* 2-(1′-*naphthoyl*)-*coumarone*-3-*carboxylate* (2.7 g.) was obtained by the action of 1-chloroacetylnaphthalene (2.1 g.) on coumaran-dione (1.5 g.) in presence of alcoholic sodium ethoxide from sodium (0.23 g.) and alcohol (20 c.c.). The compound crystallised from alcohol in colorless prismatic needles, m.p. 110°, producing a red sulphuric acid reaction. (Found: C, 76.7; H, 4.7. $C_{22}H_{16}O_4$ requires C, 76.7; H, 4.7 per cent).

On hydrolysis with aqueous alcoholic sodium hydroxide in the usual manner, the ester (2.5 g.) afforded colorless flakes of the *sodium salt* which were collected to furnish on acidification the corresponding *acid* as a yellow mass with poor crystallising habit. On three crystallisations from acetic acid, this was obtained as a yellow microcrystalline mass (1.5 g.), m.p. 145° with prolonged sintering. (Found: C, 75.2; H, 4.1. $C_{20}H_{12}O_4$ requires C, 75.9; H, 3.8 per cent).

Cyclisation.—The acid (0.5 g.) was converted into the acid chloride by leaving overnight in contact with thionyl chloride (6 c.c.). The next day, thionyl chloride was removed in vacuum, the residue dissolved in dry CS_2 and treated with $AlCl_3$ (1.6 g.). After 3 hours, the complex was decompose with ice to furnished an orange solid which after two crystallisations from acetic acid, followed by sublimation in vacuum, afforded the *quinone* in fine orange-red powder, m.p. 197°. (Found: C, 80.0; H, 3.3. $C_{20}H_{10}O_3$ requires C, 80.5; H, 3.4 per cent). The compound develops a pink coloration with H_2SO_4.

2-(*o Carboxybenzoyl*)-*coumarone*-3-*carboxylic Acid.*—Coumaran-dione (1.3 g.) was dissolved in methanolic sodium methoxide from sodium (0.22 g.) and dry methanol (10 c.c.) and treated with *o*-carbomethoxyphenacyl bromide (2.2 g.). After refluxing for 3 hours, the mixture was worked up to yield the *diester* (IV) as a gum which was directly hydrolysed with boiling aqueous alcoholic sodium hydroxide for ½ hour. Acidification after removal of the alcohol afforded a gum crystallising from acetic acid (50%) in prismatic needles (1.5 g.), m.p. 222°, giving a yellow sulphuric acid reaction. (Found: C, 66.1; H, 3.4. $C_{17}H_{10}O_6$ requires C, 65.8; H, 3.2 per cent).

Cyclisation.—The above acid was converted into the *barium salt* by the action of barium chloride on the ammonium salt. The dry salt was pyrolysed at 340°-360° for ½ hour and the product collected on a cold finger. The crude material on treatment with

acetic acid afforded a small quantity of yellow plates of β-brazanquinone, m.p. 242°, identical with an authentic specimen.

Cyclisation of 2-(o-*Carboxybenzoyl*)-*coumarone.*—The acid (0.4 g.) (this *Journal*, 1954, **31**, 104) was dissolved in H_2SO_4 (conc., 6 c.c.) and heated on a boiling water-bath for 30-35 minutes. The orange solution which had assumed a darker colour was poured on ice, the yellow precipitate collected, washed with dilute NaOH solution and filtered. The yellow precipitate of β-brazanquinone was collected, crystallised from acetic acid and obtained in yellow plates (0.11 g.), m.p. and mixed m.p. 244°. (Found: C, 77.3; H, 3.2. Calc. for $C_{16}H_8O_3$: C, 77.4; H, 3.3 per cent). The aqueous alkaline filtrate on acidification gave a gelatinous precipitate which became crystalline on warming. The product (0.07 g.) was identified as the original acid, m.p. and mixed m.p. 202-203°.

Condensation of Coumaran-dione with sym.-*Dichloroacetone.*—To a solution of coumaran-dione (9.3 g.) in alcoholic sodium ethoxide from sodium (1.5 g.) and dry alcohol (25 c.c.) was added dropwise a solution of dichloroacetone (4.0 g.) in dry alcohol (25 c.c.). After refluxing for 2 hours, the mixture was worked up next day to furnish *ethyl* 2:2′-*dicoumaronylketone*-3:3′-*dicarboxylate* (VII, R = Et) (4.5 g.), crystallising from alcohol in colorless hard prisms, m.p. 83-84°, imparting a deep red coloration with H_2SO_4. (Found: C, 67.5; H, 4.5. $C_{23}H_{18}O_7$ requires C, 67.9; H, 4.5 per cent).

On hydrolysis with aqueous alcoholic sodium hydroxide (45 c.c., 5%), this ester (4.0 g.) furnished the corresponding *acid* (2.8 g.) obtained as a brownish mass which after repeated crystallisations from aqueous acetic acid, was obtained in yellow wooly mass, m.p. 246°. (Found: C, 64.9; H, 3.0. $C_{19}H_{10}O_7$ requires C, 65.2; H, 2.9 per cent).

2:4-*Dinitrophenylhydrazone* crystallised from alcohol in deep red prisms, m.p. 279-80° (decomp.). (Found: N, 10.2. $C_{25}H_{14}O_{10}N_4$ requires N, 10.6 per cent).

Attempted Cyclisation.—The foregoing acid on treatment with acetic anhydride gave none of the expected anhydro dilactone (cf. Mayer, *loc. cit.*) in a crystalline condition. The reaction mixture on exposure gave the original acid by hydration. On heating the acid at 240°-260° and collecting the volatile products in vacuum on a cold finger, a copious yield of colorless needles, mixed with a little orange-red product, was obtained. On heating with sodium bicarbonate, the colorless product went into solution leaving an insignificant quantity of the orange-red material. The product is probably the quinone (VIII) as its colour in acetic acid is rapidly discharged on addition of zinc dust. The bicarbonate solution, on acidification, gave the colorless product, crystallising from benzene-light petroleum in colorless prisms, m.p. 162°. The product developed no coloration with H_2SO_4. (Found: C, 64.2; H, 3.6 per cent). On boiling with alkali for a few minutes, followed by precipitation with HCl, a yellowish product was obtained, crystallising from acetic acid (90%) in yellowish needles, m.p. 158°, undepressed on admixture with the original colorless material but giving a pinkish red coloration with H_2SO_4.

Condensation of Coumaran-dione with 2-*Bromoacetylcoumarone.*—2-Bromoacetylcoumarone (2.4 g.) was condensed with coumaran-dione (1.5 g.) in alcoholic sodium ethoxide from sodium (0.23 g.) and alcohol (15 c.c.) in the usual manner. The product,

ethyl 2:2'-dicoumaronyiketone-3-carboxylate (X, R=Et), was obtained in brownish prisms, m.p. 116-17°, developing an orange red coloration with H_2SO_4; yield 80%. (Found: C, 72.3; H, 4.2. $C_{20}H_{14}O_5$ requires C, 71.8; H, 4.2 per cent).

The above ester (1.8 g.) was hydrolysed by dissolving it in alcohol (20 c.c.) and warming it for a few minutes with 10% NaOH solution (6 c.c.), when the colorless *sodium salt* separated copiously at once. On acidification, the yellow crystalline acid (X, R=H) separated, crystallising from acetic acid in yellow wooly mass (1.2 g.), m.p. 228°. (Found: C, 71.0; H, 3.2. $C_{18}H_{10}O_5$ requires C, 70.6; H, 3.2 per cent).

The 2:4-*dinitrophenylhydrazone* crystallised from a large volume of alcohol in orange-red mass, m.p. 294° (decomp.). (Found: N, 11.2. $C_{24}H_{14}O_8N_4$ requires N, 11.5 per cent).

Cyclisation of (X, R=H): *Formation of Benzo*-bis [1:2-b, 5:4-b']-*benzofuran*-6:12-*dione* (VIII).—The foregoing acid (X, R=H) (0.4 g.) was converted into the acid chloride by the addition of thionyl chloride (2 c.c.) and leaving the mixture overnight. The next day, thionyl chloride was removed and replaced by dry CS_2 (15 c.c.). To the cooled solution $AlCl_3$ (1.0 g.) was added with stirring and the mixture left at room temperature for 1½ hours. After careful decomposition of the aluminium complex, the orange-red mass was extracted with warm acetic acid (3 × 10 c.c.) and then concentrated to 5 c.c. Dark red crystals mixed with an amorphous mass was obtained (50 mg.). This was crystallised twice from acetic acid and finally from a small quantity of nitrobenzene, furnishing the quinone (VIII) in red leaflets (7 mg.), m.p. 273-76°, producing a pink coloration with H_2SO_4. (Found: C, 74.5; H, 2.8. $C_{18}H_8O_4$ requires C, 75.0; H, 2.8 per cent).

The compound dissolves in acetic acid imparting an orange-yellow colour which is rapidly discharged on addition of zinc dust. It is felt that if the period of reaction be shortened, a better yield of the quinone may be anticipated. Attempts to cyclise the acid (X, R=H) with H_2SO_4 gave unchanged material, while cyclisation by way of the acid chloride by the action of PCl_5 in benzene, followed by treatment with $AlCl_3$, yielded only an amorphous material.

2-(2'-Benzofuryl)-quinoline-4-carboxylic Acid (XI).—To a boiling solution of isatin (0.45 g.) in 30% aqueous KOH (3 c.c.) was added a solution of 2-acetylbenzofuran (0.5 c.c.) in alcohol (10 c.c.). After boiling for 3 hours, the mixture was diluted, filtered from a small residue and acidified. The *acid* (XI) crystallised from acetic acid in yellow needles, m.p. 290-92° (decomp.), yield 0.5 g. The compound gave a yellow coloration with H_2SO_4. (Found: C, 74.2; H, 4.0. $C_{18}H_{11}O_3N$ requires C, 74.7; H, 3.8 per cent).

o-Methoxyphenacyl chloride was prepared according to Tutin (*J. Chem. Soc.*, 1910, **97**, 2500) from anisole and chloroacetyl chloride. The separation of the *ortho* compound from its *para*-isomer was not complete by steam distillation. Mechanical separation followed by crystallisation was advantageous and the pure *ortho*-isomer was obtained in beautiful prisms, m.p. 69.5° (lit. m.p. 69°).

Condensation of Coumaran-dione with o-Methoxyphenacyl Chloride.—Coumarandione (0.4 g.) was condensed with the phenacyl chloride (0.46 g.) in alcoholic sodium ethoxide (from sodium, 0.06 g. in dry alcohol, 3 c.c.) in the usual manner. *Ethyl*

o-methoxybenzoylcoumarone-3-carboxylate was obtained from alcohol in prisms (0.43 g.), m.p. 94-95°. (Found: C, 70.3; H, 5.2. $C_{19}H_{16}O_5$ requires C, 70.4; H, 5.0 per cent).

The product on boiling with a mixture of acetic acid (1.5 c.c.) and hydrobromic acid (1 c.c., 48%) for 3 hours gave the phenolic *acid* (XII), crystallising from alcohol in yellow prisms, m.p. 164-66°, yield 80%. (Found: C, 68.0; H, 3.8. $C_{16}H_{10}O_5$ requires C, 68.1; H, 3 6 per cent). On treatment with acetic or propionic anhydride for a very short period, the product dissolved and then colorless crystals of the *lactone* (XIII) separated. The compound crystallised from acetic acid in colorless needles, m.p. 257-58°, yield 90%. (Found: C, 73.2; H, 3.3. $C_{16}H_8O_4$ requires C, 72.7; H, 3.1 per cent). Infra-red spectrum: λ_{max}^{nujol}, 2.3, 3.5, 6.8, 7.25, 8.22, 13.1, 13.82 and 15.08 μ.

Condensation of Coumaran-dione with o-Nitrophenacyl Bromide.—The condensation was effected in alcoholic sodium ethoxide in the usual manner and the product, *ethyl 2-o-nitrobenzoylcoumarone-3-carboxylate*, was obtained from alcohol in yellowish prisms, m.p. 116°, yield 74%. (Found: N, 4.2. $C_{18}H_{13}O_6N$ requres N, 4.1 per cent). Hydrolysis with aqueous alcoholic NaOH for ½ hour on the water-bath (odour of nitrobenzene) gave after acidification the related *acid*, crystallising from acetic acid in yellow needles, m.p. 194°. (Found: N, 4.4. $C_{16}H_9O_6N$ requires N, 4.5 per cent).

The acid (0.8 g.) in ammonium hydroxide was added to a solution of ferrous sulphate (9.0 g.) in water (25 c.c.); liquor ammonia (15 c.c.) was added to it and then the mixture warmed on the water-bath for 3 hours. The filtered solution was concentrated and acidified to afford *2-(o-aminobenzoyl)-coumarone-3-carboxylic acid* which was cyclised to the *amide* (XV) on treatment with warm acetic anhydride (20 c.c.). The amide which crystallised from the solution was obtained in yellow needles from acetic acid, m.p. >320°. The compound is insoluble in sodium bicarbonate solution. (Found: C, 73.0; H, 3.5. $C_{16}H_9O_3N$ requires C, 73.0; H, 3.5 per cent).

Coumaranone (cf. Bose and Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 4703) was conveniently prepared from the diazoketone derived from *o*-methoxybenzoyl chloride. The diazoketone was obtained according to the modified method of Newman and Beal (*ibid.*, 1949, **71**, 1506). The acid chloride (9.3 g.) in dry ether (20 c.c.) was added to a cooled solution of diazomethane from nitrosomethylurea (15 g.) in ether (75 c.c.) containing anhydrous triethylamine (5 g.). The next day, the flocculent precipitate of the amine hydrochloride was removed by filtration and the filtrate on concentration in vacuum at ordinary temperature yielded the crude diazoketone (*ca.* 9 g.) which was cyclised according to Bose and Yates (*loc. cit.*) to furnish pure coumaranone (6.1 g.), m.p. 101.5°.

3-Benzylcoumarone.—Coumaranone (4.0 g.) was dissolved in dry ether (50 c.c.) and added with stirring to an excess of benzylmagnesium chloride in ether. After refluxing for 1 hour, the mixture was decomposed with ice and hydrochloric acid and worked up as usual. After a small fore-run, *3-benzylcoumarone* was obtained as a

yellowish oil (2.6 g.), b.p. 170°-175°/12 mm. (Found : C, 86.0 ; H, 6.1 $C_{15}H_{12}O$ requires C, 86.5 ; H, 5.8 per cent). The material gave no picrate and gave a yellow coloration with sulphuric acid.

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SOME SUBSTITUTED PIPERIDINES AND PYRIDINES

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Several substituted piperidines and 4-piperidinols have been prepared from substituted 4-piperidones. When heated with sulphur, the piperidines undergo dehydrogenation, and the piperidinols undergo dehydrogenation as well as dehydration, affording pyridines in excellent yields.

The method of Baliah and co-workers (*J. Amer. Chem. Soc.*, 1948, **70**, 3853; this *Journal*, 1954, **31**, 250; *Curr. Sci.*, 1954, **23**, 91, 264; *Science & Culture*, 1954, **20**, 193) is convenient to prepare substituted 4-piperidones. It should be possible to convert them into a variety of piperidine and pyridine derivatives by the well-known reactions. The reduction of 4-piperidones by the Meerwein-Ponndorf-Verley method gave two isomeric 4-piperidinols, the α- and β. The formation of such isomeric alcohols is well known (cf. Jackman and Mills, *Nature*, 1949, **164**, 789; Ziering and Lee, *J. Org. Chem.*, 1947, **12**, 911). The piperidones reduced in the present investigation and the products obtained are shown in Table I.

The Wolff-Kishner reduction of the 4-piperidones furnished piperidines in good yields. Some of the piperidines, especially those having high molecular weights, were obtained as oils, and could not be obtained in a pure condition, in view of the larger quantities required; for example, 3.5-dimethyl-2:6-di-*p*-anisylpiperidine was obtained as a brown oil. These piperidines formed hygroscopic hydrochlorides and hydrobromides, and thus offered further difficulties for their characterisation. The relevant data on the piperidines prepared are recorded in Table II. The dehydrogenation of the piperidines to pyridines readily occurred when heated with sulphur. Data on the pyridines prepared by this method are shown in Table IV.

Several 4-phenyl- and 4-alkyl-4-piperidinols have been prepared by the Grignard reaction (see Table III). Some of these 4-piperidinols were treated with acetyl chloride and 4-chloropiperidines were obtained. The 4-piperidinols, when heated with sulphur, underwent dehydration as well as dehydrogenation and yielded pyridines.

Experimental

Preparation of 4-Hydroxypiperidines by the Meerwein-Ponndorf-Verley Reduction.— To 200 c. c. of an *iso*propyl alcoholic solution of aluminium (5.4 g.) (Adams, "Organic Reactions," Vol. II, 1947, p. 178) was added the 4-piperidone (0.05 *M*) in *iso*propyl alcohol (100 c. c.). The reactants were distilled through a short column and the distillate was tested frequently for acetone, using a 0.1% solution of 2:4-dinitrophenylhydrazine hydrochloride. When the reaction was complete, the excess alcohol was removed under reduced pressure and the residue in the flask was hydrolysed with ice-cold dilute hydrochloric acid (500 c. c.). After allowing it to stand overnight, the precipitated hydrochloride of the 4-hydroxypiperidine was collected on a filter. The filtrate on concentration furnished a further quantity of the substance. The base was

obtained by treating a suspension of the hydrochloride in acetone with excess of aqueous ammonia. The α- and β-forms of the base were separated by fractional crystallisation from acetone-water. The α-form was less soluble. The two forms were further recrystallised till there was no change in m. p. in each case. The α-form crystallised in needles and the β-form as flakes (Table I).

TABLE I

4-Piperidinols prepared by the Meerwein-Ponndorf-Verley reduction.

4-Piperidinol.	M. P.		Formula	% Carbon.			% Hydrogen.		
				Found.		Calc.	Found.		Calc.
	α *	β *		α.	β.		α.	β.	
2 :6-Diphenyl-	135-36°	99-101°	$C_{17}H_{19}ON$	80.7	80 8	80.6	7.7	7.5	7·5
3-Methyl-2 :6-diphenyl-	123-24°	92 93°	$C_{18}H_{21}ON$	81.1	81.1	80.9	7.7	8.1	7·9
3 :5-Dimethyl-2 :6 diphenyl-	—	110-11°	$C_{19}H_{23}ON$	—	81.6	81.1	—	8 5	8.2
1 :3 :5-Trimethyl-2 :6-diphenyl-	126-28°	90-92°	$C_{20}H_{25}ON$	81.1	81.1	81.4	8.5	8.7	8.5

* α = α-Isomer ; β = β-isomer.
† The α-isomer could not be obtained in a pure condition.

Preparation of Substituted Piperidines by the Wolff-Kishner Method.—The modified method due to Huang-Minlon (*J. Amer. Chem Soc.*, 1946, **68**, 2487; Adams, "Organic Reactions." Vol. IV, 1950, p. 391) using diethyleneglycol as a solvent was adopted. A solution of the piperidone (0.03*M*), 50% hydrazine hydrate (20 c. c.) and solid KOH (5 g.) in diethyleneglycol (100 c. c.) were refluxed for one hour and the temperature of the mixture was allowed to rise to 200° which was maintained for additional 3 hours. It was then cooled and diluted with 500 c. c. of water and extracted with five 100 c. c. portions of ether. The combined ether extracts on treatment with HCl (conc., 30 c. c.) yielded the hydrochloride of the piperidine. It was recrystallised from ethanol. The base liberated by treating a suspension of the hydrochloride in acetone with dilute ammonia was recrystallised from ethanol (Table II).

TABLE II

Substituted piperidines.

No.	Piperidine.	M. P.	Formula.	% Carbon.		% Hydrogen.	
				Found.	Calc.	Found.	Calc.
1.	2 :6-Diphenyl-	73-74°	$C_{17}H_{19}N$	86.3	86.3	7·9	8.0
2.	3-Methyl-2 :6-diphenyl-	75-76°	$C_{18}H_{21}N$	86.5	86.1	8.2	8.4
3.	* 1 :3-Dimethyl-2 :6-diphenyl-	35-36°	$C_{19}H_{23}N$	85.7	86.0	8.9	8.7
4.	3 :5-Dimethyl-2 :6-diphenyl-	56-57°	$C_{19}H_{23}N$	86.1	86.0	8.5	8.7

* Prepared from No. 2 by methylating with dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone. The *hydrochlorides* of Nos. 1, 2 and 4 had m.p. 310-11° (Found :Cl, 12.8. $C_{17}H_{19}N$. HCl requires Cl, 13 0 per cent), 326-27° (Found :Cl, 12.4. $C_{18}H_{21}N$.HCl requires Cl, 12.6 per cent), and 336-37° (Found : Cl, 11.5 $C_{19}H_{23}N$. HCl requires Cl, 11 8 per cent) respectively. The *hydrochloride* of No. 3 is hygroscopic

TABLE III

4-Piperidinols by the Grignard reaction.

No.	4-Piperidone used	Grignard reagent.	Hydrochlorides. % Yield	M.P.	% Chlorine. Found.	Calc.	Bases. M.P.	Formula	% Carbon. Found.	Calc.	% Hydrogen. Found.	Calc.
1.	2 :6-Diphenyl-	PhMgBr	84	263-64°	9.4	9.7	98-99°	$C_{23}H_{27}ON$	84.0	83.9	7.1	7.0
2.	Do	MeMgI	74	256-57°	11.8	11.7		obtained as oil.				
3.	3-Methyl-2 :6-diphenyl-	PhMgBr	81	208-10°	9.4	9.3	154-55°	$C_{24}H_{25}ON$	83.6	83.9	7.1	7.3
4.	Do	MeMgI	76	248-49°	11.0	11.2	72-73°	$C_{19}H_{23}ON$	81.6	81.1	8.5	8.2
5.	Do	EtMgI	68	313-14°	10.5	10.7		obtained as an oil.				
6.	2 :6-Di-*p*-anisyl-1 :3-dimethyl-	PhMgBr	76	189-91°	7.7	7.8	140-41°	$C_{27}H_{31}O_3N$	77.4	77.7	7.3	7.4
7.	3 :5-Dimethyl-2 :6-diphenyl-	MeMgI	83	336-37°	10.6	10.7	141-42°	$C_{20}H_{25}ON$	81.0	81.4	8.5	8.5
8.	Do	EtMgI	78	332-33°	10.4	10.3	151-52°	$C_{21}H_{27}ON$	81.7	81.6	8.9	8.7
9.	Do	PrMgI	75	295-96°	9.9	9.9	70-72°	$C_{22}H_{29}ON$	81.4	81.7	9.0	9.0
10.	Do	BuMgI	73	235-36°	9.5	9.5		obtained as an oil.				

The acetate of base No. 1, prepared by the action of acetic anhydride in pyridine solution, melted at 194-96°. (Found :C, 80.7; H, 6.9. $C_{25}H_{25}O_2N$ requires C, 80.9; H, 6.7 per cent).

The acetate of No. 3 melted at 184-86°. (Found : C, 80.6; H, 6.8. $C_{26}H_{27}O_2N$ requires C, 81.1; H, 7.0 per cent).

The acetate of No. 8 melted at 183-84°. (Found: C, 78.3; H, 8.1. $C_{21}H_{29}O_2N$ requires C, 78.6; H, 8.3 per cent).

Preparation of 4-Piperidinols by the Grignard Reaction.—To an ice-cold solution of the Grignard reagent, prepared from 0.1 g. atom of magnesium, was added 0.02 to 0.03 mole of the piperidone, dissolved in dry ether. The reaction was completed by boiling the solution for 30 minutes. The complex was then decomposed with cold dilute HCl and the precipitated hydrochloride of the 4-piperidinol was recrystallised from water. The base was liberated as usual (Table III).

Dehydrogenation of Piperidines and 4-Piperidinols.—The piperidine or 4-piperidinol (0.02*M*) was intimately mixed with finely powdered sulphur (4 g.) and taken in a thin-walled test tube. It was heated in an oil-bath maintained at 200° for 30 minutes, cooled and then extracted several times with ether. On evaporation of the ether, the pyridine was obtained which was recrystallised from ethanol (Table IV).

TABLE IV

Substituted pyridines.

No.	Pyridine.	% Yield.	M.P.	Formula.	% Carbon		% Hydrogen.	
					Found.	Calc.	Found.	Calc.
1.	2 :6-Diphenyl-(*a*)	92	81-82°	...	...	...	...	...
2.	3-Methyl-2 :6-diphenyl-(*b*)	85	84-85°	...	...	...	..	...
3.	3 :5-Dimethyl-2 :6-diphenyl-(*c*)	88	134-35°	$C_{19}H_{17}N$	87.7	88.0	6 9	6.6
4.	2 :4 :6-Triphenyl-(*d*)	95	134-36°	—	...	...	...	...
5.	3-Methyl-2 :4 :6-triphenyl-	85	137-38°	$C_{24}H_{19}N$	89.4	89.7	6.2	5.9
6.	3 :-5Dimethyl-2 :4 :6-triphenyl-(*e*)	94	155-56°	$C_{25}H_{21}N$	89.4	89.6	6.7	6.3
7.	3 :4 :5-Trimethyl-2 :6-diphenyl-	92	116-17°	$C_{20}H_{19}N$	88.2	87.9	6.6	7.0
8.	4-Ethyl-3 :5-dimethyl-2 :6-diphenyl-(*f*)	90	109-10°	$C_{21}H_{21}N$	88.2	87.8	7.5	7.3
9	3 :5 Dimethyl-2 :6 diphenyl-4-propyl-(*g*)	90	124-25°	$C_{22}H_{23}N$	87.8	87 7	7.6	7.6
10.	4-Methyl-2 :6-diphenyl-(*h*)	80	73-74°	...	...	...	...	...
11.	2 :6-Di-*p*-anisyl-3 :5-dimethyl-4-phenyl-	99	167-68°	$C_{27}H_{25}O_2N$	81.8	82.0	6.7	6.5

(*a*) Scholtz (*Ber.*, 1895, **28**, 1731) and Pall and Strasser (*Ber.*, 1887, **20**, 2764) report m.p. 81-82°. The platinic chloride salt melted at 194-96° after recrystallisation from water. Scholtz, Strasser *et al.* (*loc. cit.*) report m.p. 205°.

(*b*) Scholtz (*Ber.*, 1899, **32**, 1939) reports b.p. 253-55°/25 mm. Its mercuric chloride salt melted at 158-60°; Scholtz (*loc. cit.*) reports m.p. 160°.

(*c*) The platinic chloride salt melted at 231-34°.

(*d*) Reddlein (*Ber.*, 1920, **53**, 334) reports m.p. 135-36°; Frank and Seven (*J. Amer. Chem. Soc.*, 1949, **71**, 2629) report m p. 137-38°, and Weiss (*ibid.*, 1952, **74**, 200) reports m.p. 137.5°. Its picrate melted at 194-95°; Reddlein (*loc. cit.*) reports m.p. 192-95°.

Preparation of 4-Chloro-3-methyl-2:4:6-triphenylpiperidine.—To 4-hydroxy-3-methyl-2 : 4 : 6-triphenylpiperidine (3 4 g., 0.01 *M*) was added 5 c. c. (excess) of acetyl chloride. After ½ hour, the mixture was poured into water and treated with dilute ammonia till alkaline. The precipitated substance crystallised from ethanol as tiny needles, m.p. 129-31°, yield 3.2 g. (85%). (Found : C, 79.3; H, 6.8. $C_{24}H_{24}NCl$ requires C, 79.7; H, 6.6 per cent).

4-Chloro-3:5-dimethyl-2 : 4 : 6-triphenylpiperidine was obtained according to the foregoing procedure from 4-hydroxy-3 : 5-dimethyl-2:4:6-triphenylpiperidine in 82% yield. Recrystallisation from ethanol gave needles, m.p. 138-39°. (Found: C, 79.5; H, 7.1. $C_{25}H_{24}NCl$ requires C, 79.9; H, 6.9 per cent).

(*e*) Its picrate, recrystallised from benzene, melted at 237-38°. (Found :C, 66.5; H, 4.2. $C_{31}H_{23}O_7N$ requires C, 66.1; H, 4.1 per cent).

(*f*) Its platinic chloride salt, recrystallised from water, melted at 205-208°. (Found : C, 50.9; H, 4.6. $C_{42}H_{46}N_2PtCl_6$ requires C, 51.1; H, 4.7 per cent).

(*g*) Its platinic chloride salt, recrystallised from water, melted at 184-82°. (Found : C, 52.0; H, 4.6. $C_{44}H_{48}N_2PtCl_6$ requires C, 52.2; H, 4.7 per cent).

(*h*) Dilthey (*J. prakt. Chem.*, 1916, **94**, 74) reports m.p. 72-73°.

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ORGANIC SULPHUR COMPOUNDS. PART I. REACTIONS OF BENZOYL AND *bis-p*-NITROBENZOYL DISULPHIDES WITH DIFFERENT BASES

By Kazi Abdul Latif and Mohammad Anwarul Azim

Attempts have been made for synthesising sulphur analogue of perbenzoic acid by the action of sodium methoxide on benzoyl disulphide, but under the conditions studied it could not be isolated.

Evidence has been put forward in support of a mechanism of cleavage of benzoyl disulphide in basic medium with the rupture of C–S bond in preference to the S–S bond.

Though oxygen and sulphur are in the same group in the Periodic Table, analogous compounds of oxygen and sulphur sometimes show marked difference in physical and chemical properties, and it is not always possible to predict the properties of one class of compounds if those of the other class are known. Benzoyl disulphide (PhCO-S.S-COPh) is partially a sulphur analogue of benzoyl peroxide, and though the latter compound has been studied fairly extensively, not many of the reactions of the former are known (Beilstein, "Handbuch der Organische Chemie", Vol. IX, p. 428 ; *Chem. Abs.*, 1936, **30**, 8189 ; 1940, **34**, 4062).

Benzoyl peroxide is known to react with sodium methoxide to yield sodium salt of perbenzoic acid and methyl benzoate (Braun, "Organic Syntheses," Coll. Vol. I, p. 431); but apparently the reaction of benzoyl disulphide with pure sodium methoxide has not been studied. With alcoholic KOH, however, it is reported to yield benzoic acid, thiobenzoic acid and sulphur (Fromm, *Ber.*, 1907, **40**, 2863). With sodium methoxide, benzoyl disulphide might react in either of the following ways :

$$PhCO.S.S.COPh + NaOMe \longrightarrow PhCO.SNa + PhCO.S.OMe \quad (I)$$

$$PhCO.S.S.COPh + NaOMe \longrightarrow PhCO.S.SNa + PhCO.OMe \quad (II)$$

Fromm (*loc. cit.*) in explaining the reaction of alcoholic KOH on benzoyl disulphide postulated a mechanism of addition of the base to the carbonyl group and cleavage of the C—S bond (as in II above). The relative bond energies of C—S and S—S are 54.5 and 63.8 k cal. respectively (Pauling, "The Nature of Chemical Bonds", 2nd Ed., Cornell University Press, New York, 1945, p. 53), but data of Franklin and Lumpkin (*J. Amer. Chem. Soc.*, 1952, **74**, 1023) show that sometimes the two values may be equal. If the cleavage takes place by the mechanism (II), as shown above, sulphur analogue of perbenzoic acid (PhCO.S.SH) may be obtained under certain conditions.

When benzoyl disulphide was allowed to react with sodium methoxide, only thiobenzoic acid, methyl benzoate and sulphur were obtained, and no sulphur analogue of perbenzoic acid could be isolated. The aqueous solution immediately after the reaction was found to contain sodium thiobenzoate. Now the question is whether thiobenzoic acid is formed directly by the cleavage of the S—S bond as shown in (I) or it results from the transient formation of PhCO.S.SNa by the mechanism (II). That the

cleavage takes place according to the mechanism (II) is evident through the study of (*a*) the effect of bases of different basicity on the cleavage of benzoyl disulphide and also (*b*) comparison of the reactivity of benzoyl and *bis-p*-nitrobenzoyl disulphides towards the same base. If the reaction is initiated by an attack of the base on the carbonyl carbon atom, the yield of the thiobenzoic acid should increase with increased basicity of the base used. This was found to be the case as shown in Table I.

TABLE I

Reaction of benzoyl disulphide with sodium alkoxides.

Time of reaction = 30 mins.
Temp. = 10°

	Base used.	% Yield of thiobenzoic acid.
Increased basicity ↓	CH_3ONa	86.5
	C_2H_5ONa	90.1
	$n.C_3H_7ONa$	93.2

TABLE II

Reaction of benzoyl disulphide with aromatic bases.

Temp. = 50°.

	Base used.	% Yield of the product.
Increased basicity ↓	*p*-Nitroaniline	No reaction *
	Aniline	75
	p-Toluidine	95

When aromatic bases like aniline, toluidine etc. were used, corresponding anilides were obtained, and S and H_2S were liberated, but the yield of the product was in conformity with the basicity of the base used as shown in Table II.

On the other hand, if the positive character of the carbonyl carbon atom in the disulphide increases (as it is in *bis-p*-nitrobenzoyl disulphide due to the strongly negative nitro group in the *para* position), the yield of the corresponding products should increase. This was also verified experimentally (Table III).

TABLE III

Comparison of the reactivity of benzoyl and bis-p-*nitrobenzoyl disulphides with the same base.*

Base used.	% Yield of the product.	
	With benzoyl disulphide.	With *bis-p*-nitrobenzoyl disulphide.
CH_3ONa (30°)	69.3	71
Aniline (50°)	75	97

All these results indicate that the cleavage of benzoyl disulphide takes place according to the mechanism (II).

EXPERIMENTAL

Benzoyl disulphide was prepared from benzoyl chloride (69.2 g., 0.5 mole) by the action of KHS (prepared by passing H_2S into a solution of 63 g. of KOH in 630 ml. of absolute alcohol till no longer alkaline to phenolphthalein) on it and treating the resultant potassium thiobenzoate with iodine (Flank and Blegen, "Organic Syntheses", 1948, Vol. 28, p.16), yield 68%, m.p. 127-28°.

* At the reflux temperature of xylene, however, the corcesponding derivative was formed in 28% yield.

bis-p-Nitrobenzoyl disulphide was prepared by Khaletskii and Yanovitskii (*Chem. Abs.*, 1950, **44**, 2952) by the action of $FeCl_3$ solution on an alcoholic solution of *p*-nitrobenzoic acid and also by Gabel and co-worker (*ibid.*, 1948, **42**, 4076) who prepared it by the action of sodium disulphide on *p*-nitrobenzoyl chloride (28% yield). We prepared it from *p*-nitrobenzoyl chloride by using the same procedure as was used for the preparation of benzoyl disulphide, yield 81%, m.p. 183°, agreeing with that recorded by Khaletskii *et al.* (*loc. cit.*).

Reaction of Benzoyl Disulphide with Sodium Methoxide.—In an Erlenmeyer flask, about 1.5 g. of sodium was dissolved in 30 ml. of absolute methyl alcohol with moderate cooling. The resulting solution of sodium methoxide was cooled to -5° in a freezing mixture. A solution of 15 g. of pure benzoyl disulphide in 60 ml. of chloroform was prepared, cooled to 0° and added immediately to the sodium methoxide solution with shaking and cooling at such a rate that the temperature did not rise above 0°. The addition resulted in an immediate formation of a precipitate. The addition took about 10 minutes and it was then shaken for another 20 minutes at the same temperature. The precipitate was then filtered and treated first with a little alcohol and then with water and ultimately dried, m.p. 118°. It was quite soluble in CS_2 ; it burnt with the characteristic smell of sulphur dioxide. Quantitative estimation by fusion with sodium peroxide and KOH showed that it was only elementary sulphur. It weighed 1.7 g. (96% of the theoretical amount).

The chloroform filtrate was treated with about 150 ml. of water in a separating funnel and the two layers were separated. The chloroform layer was then dried over anhydrous Na_2SO_4 and the solvent removed. The residual liquid was distilled under reduced pressure using a small efficient fractionating column. It distilled at 75°-80°/3-5 mm. (b.p. by micro method recorded 197°/760 mm.) ; $n_D^{29.5}$, 1.5108 (agreeing with the literature value for methyl benzoate). When an alcoholic solution of this substance was saturated with ammonia, allowed to stand for 2 days and then the alcohol evaporated off, crystals of benzamide came out, m.p. 128° (mixed m.p. with an authentic sample of benzamide).

The aqueous layer, as obtained above, was then treated with cold 1*N*-H_2SO_4 when a precipitate was obtained. The mixture was shaken three times with small amounts of cold chloroform. The chloroform extracts were collected together, washed with fresh water and then dried over anhydrous Na_2SO_4. On removing the solvent under reduced pressure, a liquid, acidic to litmus, was obtained which was allowed to stand overnight when crystals appeared, m.p. 125-26° (mixed m.p. with an authentic sample of benzoyl disulphide, 127°). This shows that the acidic liquid was thiobenzoic acid (which ultimately gave benzoyl disulphide by atmospheric oxidation).

The aqueous extract (before acidification with H_2SO_4) was also treated with potassium ferricyanide, because the latter was found to be a good reagent for detecting the presence of thiobenzoic acid (Formm, *loc. cit.*). There was immediate formation of benzoyl disulphide showing thereby that the aqueous solution contained sodium thiobenzoate. From the amount of benzoyl disulphide obtained back, the extent of cleavage of benzoyl disulphide was found out.

Reactions with other alkoxides were carried out similarly.

Reaction of bis-p-*Nitrobenzoyl Disulphide with Sodium Methoxide.*—This compound being much less soluble in chloroform, 115 ml. of the solvent had to be used for each 1.5 g. of the substance and the rest of the procedure was the same.

Reaction of Benzoyl Disulphide with Aniline.—Benzoyl disulphide (4 g.) was suspended in about 60 ml. of dry benzene and pure redistilled aniline (2.7 g.) was added. The mixture was then warmed to 50° for 15 minutes when H_2S gas was liberated. On cooling, a precipitate came out which was filtered off and treated with alcohol. Some insoluble residue (0.42 g.) remained behind, m.p. 118°. All tests showed that it was elementary sulphur (90% of the theoretical).

Benzene was evaporated off when crystals came out. On recrystallisation from alcohol, benzanilide came out, as confirmed by mixed m.p. with an authentic sample of benzanilide.

Similar experiment was carried out using *p*-toluidine. With *p*-nitroaniline, however, there was no reaction under identical condition. By using xylene as a solvent and carrying out the reaction at the reflux temperature for one hour, 28% of the corresponding derivative was formed.

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STUDIES ON *S*-BENZYLTHIOURONIUM CHLORIDE

By Prithwi Nath Bhargava and Shiva Mohan Verma

S-Benzylthiouronium chloride has been crystallised in two isomeric forms, exhibiting dimorphism. Interaction with potassium bromide and potassium iodide has furnished *S*-benzylthiouronium bromide and *S* benzylthiouronium iodide, which have formed addition products with mercuric chloride. *S*-Benzylthiouronium chloride has been found to be a good reagent for the identification of some specific sulphonic acids.

Bernthsen and Klinger (*Ber.*, 1879, **12**, 574) reported the reaction of benzyl chloride upon thiocarbamide. Werner (*J. Amer. Chem. Soc.*, 1890, **57**, 285) isolated the crystals of *S*-benzylthiouronium chloride by condensing benzyl chloride and thiourea in presence of alcohol in two forms, m.p. 174° and 142-43°, thus showing the possible case of dimorphism. The lower melting form, he could isolate on three occasions only according to his statement, "I find the substance purified as above (recrystallisation from alcohol or ether) to melt at 174° (uncor.) from numerous determinations, at the same time I have noticed specimens on three occasions to melt at 142-143°, a temperature which was independent of the rate of heating and was never exhibited a second time." The authors therefore, in order to isolate the two types of crystals of *S*-benzylthiouronium chloride and study its application in the identification of some specific sulphonic acids, have synthesised it. During isolation of the two forms of crystals it has been observed that the difference in the concentration of hydrochloric acid used for recrystallisation is not the cause of their formation, but the temperature has been the predominating factor. Thus parallelopiped crystals, m.p. 146-48°, have been obtained from cold dilute hydrochloric acid, and needle-shaped crystals, m.p. 174-76° from hot dilute hydrochloric acid. The mutual transformation of the parallelopiped into needle-shaped crystals has been accompli hed in the hot and the cold state respectively.

Lecher *et al.* (*Annalen*, 1924, **438**, 169 ; 1925, **445**, 35) gave a salt-like structure to *S*-benzylthiouronium chloride. The chloride anion of the compound has been substituted by bromine and iodine by using potassium bromide and potassium iodide respectively, but no dimorphism has been exhibited in the latter two halides. The bromide and iodide gave an addition product with mercuric chloride as mercurihalide, $(C_8H_{11}N_2S)X.\ HgCl_2$ (where X = Br or I).

S-Benzylthiouronium chloride has been proved to be a good reagent for the identification of *p*-nitrobenzenesulphonic acid, 2 : 5-dichlorobenzenesulphonic acid, 1 : 4-sulphanilic acid, α-naphthylamine-5-sulphonic acid and 2 : 6-naphthylamine sulphonic acid.

Experimental

S-Benzylthiouronium Chloride.—Benzyl chloride (120 g.), thiourea (76 g.) and alcohol (200 c.c.) were refluxed on a water-bath for one and half hours. On cooling, the product crystallised and was recrystallised from cold dilute hydrochloric acid in

parallelopiped crystals, m.p. 146-48° and from hot dilute hydrochloric acid in needle-shaped crystals, m.p. 174-76°. [Found (parallelopiped) : Cl, 17.62 ; S, 15.88 ; (needle shaped) : Cl, 17.60; S, 15 90. Calc. for $C_8H_{11}N_2SCl$:Cl, 17.56 ; S, 15.84 per cent].

S-Benzylthiouronium Bromide and Iodide.—S-Benzylthiouronium chloride (10 c.c. of 30% aq. soln.) was warmed with saturated solutions of potassium bromide (1.5 g.) and potassium iodide (2 g.) separately to 80°. On cooling, colorless crystals were obtained The crystals of bromide and iodide on recrystallisation from absolute alcohol melted at 127-28° and 140° respectively. (Found : Br, 32.31. $C_8H_{11}N_2SBr$ requires Br, 32.8 per cent) (Found : I, 43.04. $C_8H_{11}N_2SI$ requires I, 43.18 per cent).

S-Benzylthiouronium Bromide Mercurichloride.—To *S*-benzylthiouronium bromide (10 c.c. of 20% aq. soln.) mercuric chloride (2.5 g. in 30 c.c. of water) was added and warmed. On cooling, crystals were obtained, m.p. 98°. (Found : Hg, 38.88. $C_8H_{11}N_2SBr.HgCl_2$ requires Hg, 38.68 per cent).

S-Benzylthiouronium Iodide Mercurichloride.—To *S*-benzylthiouronium iodide (1 g. in 10 c.c. of water), kept in a freezing mixture, mercuric chloride (1 g. in 50 c.c. of water) was slowly added dropwise to avoid the formation of mercuric iodide. The compound crystallised on the inner side of the vessel in flowery crystals, m.p. 104°. (Found : Hg, 35.52. $C_8H_{11}N_2SI.HgCl_2$ requires Hg, 35.40 per cent).

Condensation of S-Benzylthiouronium Chloride with Sulphonic Acids.—The acid (0.01 equiv.) was dissolved in water (10 c.c.) and neutralised with $N-NaOH$ in the presence of phenolphthalein. To this S-benzylthiouronium chloride (2g. in 10 c.c. of water) was added and stirred, when a precipitate of *S*-benzylthiouronium salt of sulphonic acid was obtained. It was filtered, washed with cold water, dried and crystallised from alcohol. The melting points of *S*-benzylthiouronium salts of several sulphonic acids and percentage of sulphur are recorded in Table I.

TABLE I

Sulphonic acid.	M.P. of *S*-benzylthiouronium salt.	% Sulphur. Found.	Calc.
p-Nitrobenzenesulphonic acid	166°	17.45	17.32
2 :4-Dichlorobenzenesulphonic acid	168°	16.52	16.34
1 :4-Sulphanilic acid	189°	18.54	18.50
1 :5-Naphthylamine sulphonic acid	181°	10.74	10.63
2 :6-Naphthylamine sulphonic acid	172°	10.72	10.63

Thus the above sulphonic acids can be readily identified.

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SPECTROPHOTOMETRIC DETERMINATION OF TANTALUM

By B. Sarma and J. Gupta

A spectrophotometric method for the determination of tantalum in semi-micro quantities up to a maximum of 200 ppm has been described. Tantalum in acidified ammonium oxalate solution forms with catechol (pyrocatechol) a deep yellow complex with a high absorbancy in the near ultraviolet region. Niobium, though it forms a yellow colour with catechol in a neutral or alkaline medium, does not interfere with the estimation of tantalum over a wide range of acidity. Titanium, which forms a deep brown complex with catechol, interferes with the estimation. Anions like phosphate, fluoride and tartrate discharge the colour of the tantalum-catechol complex, whereas oxalate, sulphate, chloride etc. are without effect. Optical densities have been measured at 385 and 395 mμ.

In a mixture of the earth acids, the estimation of niobium in presence of tantalum or *vice versa* has been a difficult problem. Of the recent spectrophotometric methods, the one reported by Dinnin (*Anal. Chem.*, 1953, **25**, 1803) for estimating tantalum as the pyrogallol complex appears to be the most satisfactory. The pyrogallic acid method by Hunt and Wells (*Analyst*, 1954, **79**, 345) shows some interference caused by niobium, for which a correction factor is applicable.

Rosenheim and Roehrich (*Z. anorg. Chem.*, 1932, **204**, 342) described some complexes of niobium and tantalum with pyrocatechol. Tantalum imparts a pure yellow colour in acid media, which is stable in presence of oxalic acid and has an absorption maximum at 395 mμ. About 40 ppm of tantalum in solution can be easily detected visually. The present paper describes a spectrophotometric method for the estimation of 10-200 ppm of tantalum in an oxalic-sulphuric-hydrochloric acid mixture of normality 0.2 – 2.0. There is no interference from niobium. Titanium shows a serious interference, which can be minimised, however, by working at an acidity of 1.5 to 2*N*.

The interference from titania, invariably associated with columbites and tantalites, is a common feature of most of the colorimetric and gravimetric methods for niobium and tantalum. A nearly pure sample of earth acids can be quantitatively isolated from a complex mineral by the method of Alimarin and Frid (*Chem. Abs.*, 1945, **39**, 3751). Small amounts of titania can be separated from earth acids as sodium titanyl salicylate by the method of Schoeller and Jahn (*Analyst*, 1932, **57**, 72).

In the present investigation, pure titanium-free oxides were fused with 10 to 15 times their weight of potassium bisulphate (reagent grade) and extracted with saturated ammonium oxalate to make stock solutions of approximately 2-3% w/v. The p_H of these solutions varied between 3 and 4.

Experimental

Pure tantalum pentoxide (Johnson Matthey & Co.) was fused with twelve times its weight of potassium bisulphate (A.R.) in a silica crucible. The melt was cooled, extracted with saturated ammonium oxalate (C.P.) solution and made up to volume. The tantalum content was estimated gravimetrically with tannic acid. From the stock solution (2-3 mg. Ta per c.c.) appropriate dilutions were made with distilled water.

A standard solution of niobium (2-3 mg. Nb/per c.c.) was made similarly from pure niobium pentoxide (Johnson Matthey & Co.).

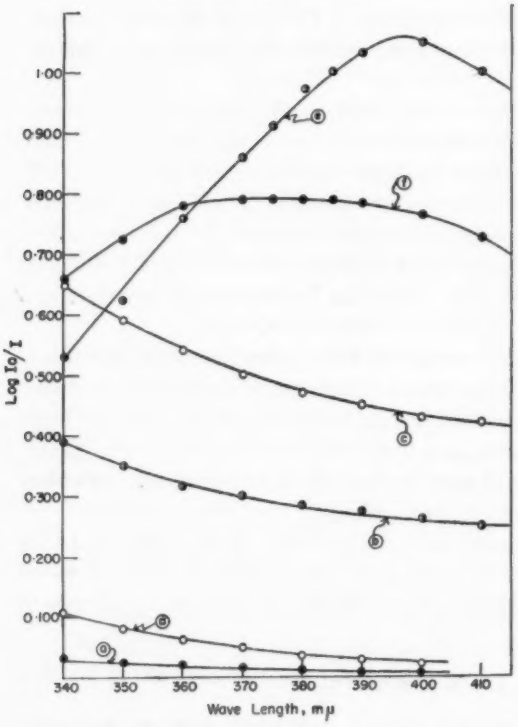
A standard solution of titanium (2-3 mg. Ti per c.c.) was prepared from a pure sample of titanium dioxide by an identical procedure.

The reagent catechol, of B.P. quality, was recrystallised from hot toluene (Organic Synthesis", Col Vol. 1, 2nd Ed., p. 149, John Wiley, New York, 1941) to give almost colorless crystals, m.p. 102-104° (lit. m.p. 103-105°). Approximately a 10% solution was made in distilled water.

A Beckman quartz spectrophotometer (model 91-E) was used for measuring the absorption, using tungsten filament lamp as a light source, and absorption cells of 1 cm. light path. Corrections were made for all readings for compensating slight differences in optical transmission of the cells.

FIG. 1

Absorption curves.



Absorption curves.—The optical densities of 1%, 2% and 3% solutions of catechol against water as the blank in the region 340 to 410 mμ are shown in curves *a*, *b*, and *c* in Fig. 1. Curve *d* in Fig. 1 shows absorption of $M/100$-Ta_2O_5 in 2% ammonium oxalate matched against water.

Curve *e* in Fig 1 shows absorption of the tantalum-catechol complex (200 ppm of Ta=5 mg./25 c.c.) in 2% catechol solution plus 0.2*N*-HCl, matched against the same solution having no tantalum. A peak is observed at 395 mμ which is the wave-length at which all subsequent measurements have been made.

Curve *f* in Fig. 1 shows absorption of titanium-catechol complex (100 ppm of Ti=2.5 mg./25 c.c.) under identical conditions. It may be seen that the absorbancy of the titanium complex rises up to 360 mμ and then remains almost constant up to 400 mμ after which it falls off.

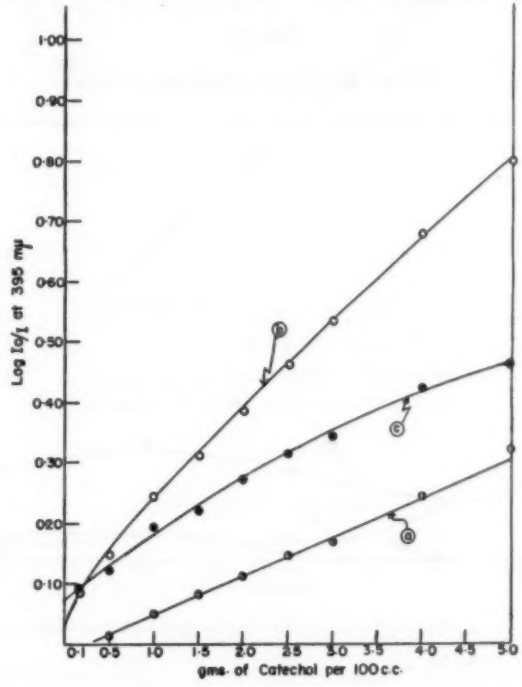
The niobium-catechol complex (200 ppm. of Nb) shows no absorbancy under similar conditions throughout the range of our study.

Effect of Time and Excess Reagent.—An aqueous solution of catechol darkened with time, but the tantalum-catechol complex was perfectly stable for over a week.

Its absorbancy, however, apparently* increased continuously with increasing reagent concentration (Fig. 2). A limit was set on the amount of catechol used because of the high absorbancy the latter produced in the blank and the correspondingly larger slit widths required for measurement. A concentration of 2% of the reagent in the final mixture was found suitable.

FIG. 2

Optical densities at different reagent concentrations.



a—Catechol in water (water as blank).
b— Do + 40 ppm Ta (water as blank).
c— Do + (catechol soln. as blank).

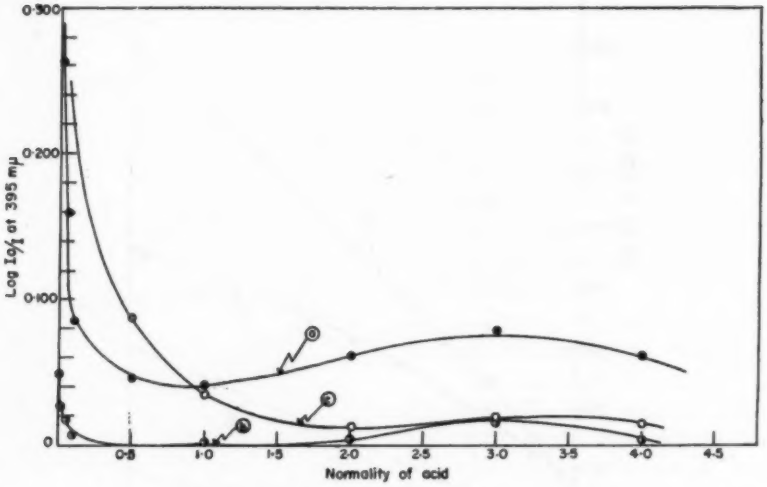
Effect of Acid.—Phosphate, fluoride and tartrate ions discharge the yellow colour of the tantalum-catechol complex, whereas perchloric and sulphuric acids tend to precipitate tantalum oxide, and nitric acid oxidises the reagent. Hydrochloric acid was found to be the most suitable, since the tantalum-catechol complex continued to show marked absorbancy at 395 mμ over a wide range of the acid concentration. Curves *a*, *b* and *c* in Fig. 3 indicate the change of absorbancy of tantalum, niobium and titanium complexes respectively with change in the concentration of hydrochloric acid in the medium.

Optical Density-concentration Curves.—Aliquots of standard tantalum solution containing 1-5 mg. Ta were taken in 25 c.c. volumetric flasks. To each were added

in succession 5 c.c. of 10% catechol solution, 5 c.c. of 1*N*-HCl and sufficient saturated ammonium oxalate solution (also containing about 3 g. of $KHSO_4$ per 100 c.c.) so that the final concentration of ammonium oxalate (and $KHSO_4$) in all the flasks attained the same value when distilled water was finally added to make up to volume. A blank solution containing all the reagents except the tantalum was also prepared. Absorbancies of the solutions at 385 and 395 mμ were determined against the blank. Curves *a* and *b* in Fig. 4 show absorbancies plotted against varying concentrations of tantalum at 395 and 385 mμ respectively. It is found that Beer's law is observed even for concentrations as high as 200 ppm of Ta.

FIG. 3

Optical densities at different acidities.



a—Ta 40 ppm in 2% catechol (2% catechol as blank).

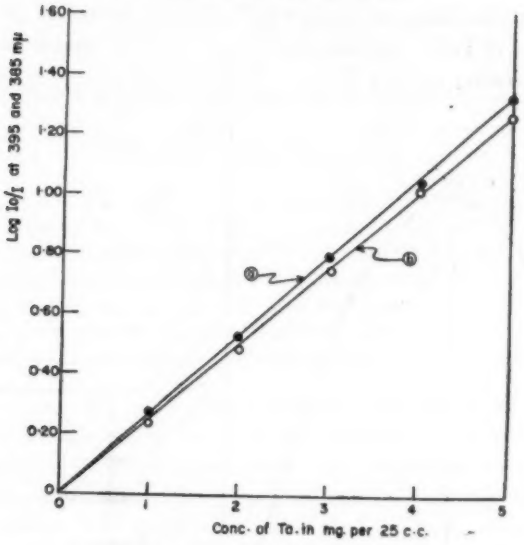
b—Nb „ „ „ Do.

c—Ti „ „ „ Do.

Estimation in presence of Niobium.—The effect of various concentrations of niobium on the estimation of tantalum was studied. About 3 c.c. of the standard tantalum solution containing 1 mg. tantalum per c.c. was taken in each of five 25 c.c. volumetric flasks, and niobium, varying from 1 to 5 mg. was added ; 5 c.c. of 10% catechol solution, 5 c.c. of 1*N*-HCl and sufficient saturated ammonium oxalate solution (also containing about 3 g. of $KHSO_4$ per 100 c.c.) were added to each of the flasks and volumes made up to 25 c.c. with distilled water. Absorbancies were measured at 385 and 395 mμ against a blank containing all the reagents except tantalum and niobium. The results recorded in Table I show that tantalum can be estimated spectrophotometrically at about 390 mμ in presence of large quantities of niobium.

FIG. 4

Beer's law curves for tantalum.



a—Densities at 395 mμ (2% catechol as blank).
b Densities at 385 mμ (2% catechol as blank).

TABLE I

Ta taken = 120 ppm.

Niobium added (ppm)	40	80	120	160	200
Ta found, ppm (at 385 mμ)	122.40	121.20	120.0	120.80	122.40
Ta found, ppm (at 395 mμ)	118 0	118 80	118 80	120.00	122.80

Interference from Ti *and other Ions.*—Titanium in a weakly acid or neutral solution interferes seriousiy with the estin ation of tantalum by forming a deep brown colour with aqueous catechol in presence of oxalate. A large number of the common ions, however, which give coloured reactions with catechol, are easily separated from tantalum in the routine procedure. Among the anions, fluoride, phosphate and tartrate interfere and should not be present in the solution.

The Composition of the Tantalum-catechol Complex.—Rosenheim and Roehrich (*loc. cit.*) isolated some green tantalum-catechol complexes with tantalum-catechol ratio 2 : 6. The composition of the yellow soluble complex formed in the present investigation was studied by Job's method (*Ann. chim.*, 1928, *x*, **9**, 113; *Anal. Chem.*, 1953, **25**, 1622) of continuous variation. The peak of the closed curve (Fig. 5) obtained by plotting optical density against increasing amounts of Ta_2O_5 in solution indicates that the yellow complex is formed when Ta_2O_5 : catechol ratio is 1 : 1. The same ratio is also obtained by the molar ratio method of Yoe *et al.* (*Ind. Eng. Chem. Anal.*

FIG. 5

Optical density-concentration curve (Job's method) for complementary mixtures of 0.9535×10^{-2} *molar solutions of* Ta_2O_5 *and catechol (total volume, 15 c.c.).*

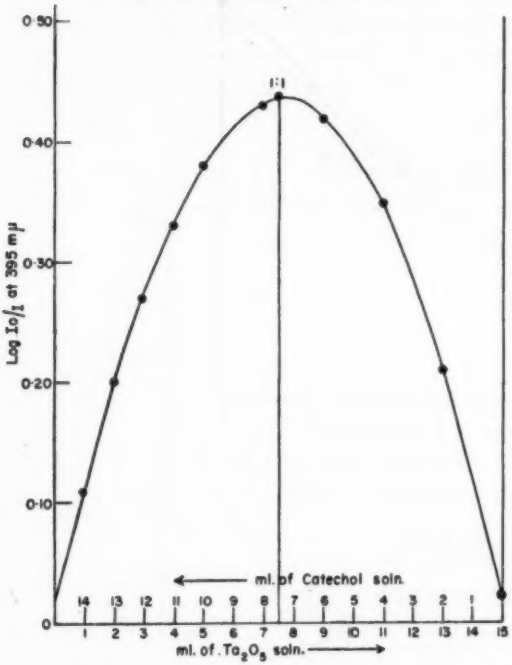
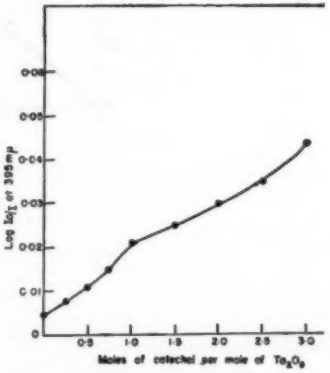


FIG. 6

Optical density-molar ratio curve for mixed solutions of Ta *(constant) and catechol.*



Ed., 1944, **16**, 111) (Fig. 6). It indicates that the yellow complex may be an oxalate-catechol complex of tantalum of the inner-metallic type.

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ON THE NATURE OF VORTMANN-FORBES' REACTION

By G. Venkateswarlu

The reaction between an acidic solution of arsenious oxide and sodium thiosulphate has been carried out in the different media e.g., HCl, HNO_3, H_2SO_4 and acetic acid. Forbes' conclusions on the variation of the period of induction with the concentrations of HCl and thiosulphate are confirmed and extended to HNO_3 and H_2SO_4. The limitations of his observations on the variation of the period of induction with the concentrations of acetic acid and arsenite are explained. The existence of the minimum period of induction at about the same acid concentration in the case of all the three mineral acids, when the concentrations of arsenious oxide and thiosulphate are kept the same, is found out.

Vortmann (*Ber.*, 1889, **22**, 2308) found arsenious sulphide to be precipitated when an acidic solution of arsenious oxide or acidified solution of an arsenite or arsenate was treated with sodium thiosulphate solution. The reaction is interesting on account of the precipitation of arsenious sulphide being preceded by a sharp and highly reproducible induction period. The reaction was later worked out by others (Weinland and Gutmann, *Z. anorg. Chem.*, 1898, **17**, 409; Mackenzie and Marshall, *J. Chem. Soc.*, 1908, **93**, 1728; Gutmann, *Ber.*, 1905, **38**, 1728, 3277; 1907, **40**, 2818; 1908, **41**, 1650; Von Szilagyi, *Z. anorg. Chem.*, 1920, **113**, 75; Forbes, Estill and Walker, *J. Amer. Chem. Soc.*, 1922, **44**, 97).

The purpose of the present work is to study the problem in greater detail in order to elucidate the nature of the mechanism for the existence of the period of induction.

Experimental

Well-cleaned glassware for use was kept overnight with chromic acid and then successively cleaned with tap-water, distilled water and finally with double-distilled water. The various chemicals used were of the reagent quality and double distilled water was used for preparing solutions. The solutions of the acids and thio were 1*N* and standardised against Na_2CO_3 (anhydrous) and standard $K_2Cr_2O_7$ in acidified KI respectively. Freshly prepared thio solution was used to avoid decomposition on storage. The arsenious oxide solution was standardised against standard iodine in presence of excess sodium bicarbonate. The same volumetric ware was used in all experiments to eliminate errors of calibration.

Each reaction requires two solutions. The A-solution contains a constant volume of the arsenious oxide solution together with required volumes of the respective acid and water, taken in a conical flask of 250 or 500 c.c. capacity, the flask being suitable for efficient mixing of the contents without spilling. The B-solution contains known volumes of sodium thiosulphate and water, the two taken in two 100 c.c. beakers separate-

ly. Whenever the water used here was large compared to that of the thiosulphate solution, some quantity of the water was transferred to the latter. In the first four sets (Tables I to IV) the acid was run from a burette and the others were measured with pipettes of appropriate capacity. To start the reaction, the thio was added to the conical flask containing the A-solution (before 3 seconds of the starting time) and the water kept in the second beaker was then transferred into the empty beaker previously containing sodium thiosulphate solution. The beaker was gently rotated to wash the sides and this wash-liquid was then transferred to the main bulk of the reaction mixture. Throughout this addition, the conical flask was vigorously rotated to ensure quick and uniform mixing. The time of the appearance of the precipitate was carefully noted with a watch. Vigorous stirring is essential to obtain reproducible results, particularly with reactants of fairly high concentrations. All the experiments were carried out at room temperature (29°-32°). The results are recorded in the following tables.

TABLE I

Expt. No.	A-solution (c c). As_2O_3 soln =25 c.c.		B-solution (c.c.) Thio soln. = 5 c c.	Period of induction (in seconds) with			
A	Water.	Acid.	Water.	H_2SO_4.	HCl.	HNO_3.	Acetic.
			Total vol. (A+B) = 75 c.c.				
1	20	0.05	25	132	145	120	150
2	20	0.1	25	112	118	110	140
3	20	0.2	25	88	90	93	125
4	20	0.5	25	81	87	75	110
5	20	1.0	25	83	92	79	97
6	20	5.0	20	165	215	162	80
7	10	10.0	25	355	555	300	75
8	10	20.0	15	630	810	...	78
			Total vol. (A+B) = 150 c.c.				
9	50	0.5	70	180	185	160	...
10	50	1.0	70	190	185	164	...
11	50	5.0	65	245	310	242	145
12	50	10.0	60	400	540	368	155
13	50	20.0	50	600	825	660	155
14	20	50.0	50	900	760	840	165
15	20	80.0	20	...	870	...	170
			Total vol. (A+B) = 225 c c.				
16	100	0.5	95	220	245	215	...
17	100	1.0	95	250	275	236	...
18	100	5.0	90	310	405	312	180
19	100	10.0	85	405	570	410	185
20	100	20.0	75	550	810	...	205

TABLE II

Expt. No. B	A-solution (c.c.). As_2O_3 soln. = 25 c.c. Water.	Acid.	B-solution (c.c.). Thio soln. = 10 c.c Water.	Period of induction (in seconds) with H_2SO_4.	HCl.	HNO_3.	Acetic.
			Total vol. (A+B) = 75 c.c.				
1	20	0.05	20	62	80	78	95
2	20	0.1	20	55	63	68	95
3	20	0.2	20	47	49	58	85
4	20	0.5	20	37	39	43	67
5	20	1.0	20	36	35	30	62
6	10	5.0	25	42	42	40	43
7	10	10.0	20	60	72	46	40
8	10	20.0	10	80	185	..	41
			Total vol. (A+B) = 150 c.c.				
9	50	0.5	65	87	79	83	...
10	50	1.0	65	83	73	75	106
11	50	5.0	60	92	90	84	90
12	50	10.0	55	120	148	99	85
13	50	20.0	45	165	255	...	78
			Total vol. (A+B) = 225 c.c.				
14	100	0.5	90	125	117	102	...
15	100	1.0	90	116	113	78	130
16	100	5.0	85	128	132	128	125
17	100	10.0	80	158	185	168	125
18	100	20.0	70	212	210	...	90

TABLE III

Expt No. C	A-solution (c.c.). As_2O_3 soln. = 25 c.c. Water.	Acid.	B-solution (c.c.). Thio soln. = 20 c.c. Water.	Period of induction (in seconds) with H_2SO_4.	HCl.	HNO_3.	Acetic.
			Total vol. (A+B) = 75 c.c.				
1	10	0.05	20	42	47	47	55
2	10	0.1	20	37	35	40	50
3	10	0.2	20	30	27	31	46
4	10	0.5	20	20	20	23	35
5	10	1.0	20	17	15	20	28
6	10	5.0	15	12	15	14	20
7	10	10.0	10	5	13	11	18
8	5	20.0	5	12	18	...	21
			Total vol. (A+B) = 150 c.c.				
9	50	0.5	55	38	...	42	60
10	50	1.0	55	32	35	36	52
11	50	5.0	50	25	33	31	42
12	50	10	45	17	31	28	39
13	50	20	35	24	34	46	34
14	20	50	35	92	127	135	31
15	20	60	25	122	147	165	32
16	10	80	15	160	172	...	32
17	5	90	10	180	...	...	32
			Total vol. (A+B) = 225 c.c.				
18	100	0.5	80	55	...	63	65
19	100	1.0	80	50	50	56	67
20	100	5.0	75	42	41	50	65
21	100	10.0	70	36	41	49	56
22	100	20.0	60	32	38	...	54

DISCUSSION

Forbes' conclusions (*loc. cit.*) are that the period of induction is strictly in inverse proportion to the thio concentration and practically independent of the concentration of the arsenite or acetic acid ; HCl prolongs the induction period. In the present study, the effect of HCl in prolonging the period of induction has been confirmed, and this property has been found to be manifested by HNO_3 and H_2SO_4 also. Our results point out the existence of a minimum period of induction for increasing values of acid concentration, when those of arsenious oxide and thio are kept constant, not previously observed by others ; the occurrence of the minimum period of induction is at the same acid concentration in the case of the various mineral acids and at a different acid concentration in the case of acetic acid. The latter is probably due to the bufferring effect of the sodium acetate which is one of the products of the reaction, in presence of the weak acetic acid. The most probable reason for Forbes' conclusion that there is practically no effect of acetic acid concentration on the period of induction is due to the use of sodium arsenite in his experiments and it yields equivalent quantities of sodium acetate which buffers the mixture and counteracts the increase of p_H with increase in the acid concentration. This fact can be verified from the present work. Though the acid is increased from 50 to 90 c.c. out of a total volume of 150 c.c. of the reaction mixture, the period of induction is constant at 32 seconds in the case of acetic acid, where 20 c.c. of sodium thiosulphate is used for each reaction affording appreciable quantity of sodium acetate. In the other first two sets of experiments, the volume of sodium thiosulphate used is only 5 c.c. and 10 c.c., and so the effect is not so pronounced. This conclusion is also in agreement with the observation of Forbes that the quantity of arsenious sulphide precipitated in the first 15 minutes is greater in the case of HCl than in the case of acetic acid. Our results although confirm Forbes' observation, that the period of induction is not a coagulation-time effect as it is not affected by excess acetic acid (or any other acid) or by aluminium salts, but do not support his view on the independence of the induction period on the concentration of either HCl or acetic acid when H^+−ion concentration is below half the concentration of sodium thiosulphate.

Separate experiments were conducted to study the period of induction with two solutions of arsenious oxide of differrent concentrations in H_2SO_4 and HCl media. Keeping the concentrations of acid and thiosulphate constant, it was found that greater the concentration of the arsenious oxide, the greater was the period of induction. This militates against Forbes' conclusions on the virtual independence of the induction period of the concentration of arsenious oxide. The occurrence of the minimum period of induction at the same acid concentration, irrespective of the variation of the concentration of the arsenious oxide in the two sets of reactions (Table IV), has also been observed with this set of reactions. Forbes' experiments are not in accord with the above observation.

Another set of experiments has been carried out to verify whether the period of induction is inversely proportional to the sodium thiosulphate concentration when the

concentrations of the acid and arsenious oxide are kept constant; and it has been found that the above observation of Forbes is true qualitatively.

The precipitation of arsenious sulphide does not take place in neutral solution. Even when a single drop of acid is added to the reaction mixture, arsenious sulphide is formed after the initial period of induction. The reaction is reversible in alkaline medium, and hence the hydrogen ion is absolutely essential for the reaction. When a large excess of acid is added, a number of individual particles (probably sulphur) are observed before the general precipitation of arsenious sulphide. The smell of sulphur dioxide was noted almost from the beginning of the reaction. The smell of hydrogen sulphide was not noted under the conditions of the experiments carried out. Effect of dilution is usually to prolong the period of induction; but in a few cases, there is no appreciable increase of the period due to dilution, or there is a tendency to shorten the same. From this it is quite reasonable to assume the existence of at least two reactions besides the immediate formation of thiosulphuric acid, one of which is predominant in dilute solutions and the other at higher concentrations.

TABLE IV

Total vol. = 75 c.c. As_2O_3 in A-solution = 25 c.c. Thio in B-solution = 5 c.c.

Expt. No. D	Vol. of the respective acid.	Period of induction (in seconds) with HCl.		with H_2SO_4	
		As_2O_3 Soln. I 0.47N.	As_2O_3 Soln. 0.19N.	As_2O_3 Soln.-II 0.47N	As_2O_3 Soln.-I 0.19N
1	0.05 c.c.	160	145	140	132
2	0.1	115	115	120	112
3	0.2	102	90	100	88
4	0.5	95	87	95	81
5	1.0	98	92	100	83
6	5.0	315	215	260	165
7	10.0	1065	540	725	355
8	20.0	1875	810	1320	630

It has already been pointed out that the occurrence of the minimum period of induction is almost at the same acid concentration in the case of the three mineral acids in each set of experiments. An analysis of the ratios of the concentrations of the reacting substances under the conditions of the minimum period of induction shows that for a constant arsenious oxide concentration of 4.75 gram equivalents, the ratios of the concentrations of acid and thiosulphate in gram equivalents are as 1 : 5, 1 : 10 and 1 : 2. In other words, the above conditions are the most suitable for the maximum velocity of reaction or minimum period of induction. Even when the concentration of arsenious oxide is varied (4.75 and 11.75), the minimum period occurs when the ratio of the concentrations of acid and sodium thiosulphate is as 1 : 10, both in the case of HCl and H_2SO_4.

Experiments done separately show that the period of induction is prolonged when part of the water medium is substituted by organic solvents like ethyl alcohol and acetone. This can only be interpreted as the effect of solvent on the course of the reaction but not the effect of alcohol or other solvents stabilising the colloidal sulphur.

Further work is in progress.

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ON THE TEMPERATURE VARIATION OF VISCOSITY OF LIQUIDS

By Shashanka Shekhar Mitra

An equation connecting the viscosity of a liquid with temperature has been derived from the concept of free volume in a liquid. The proportionality of fluidity with free space offers an equation of the type

$$\eta = \left(A + \frac{B}{T} + CT\right)^3$$

and is fairly applicable to non-associated pure liquids over wide temperature ranges. For associated liquids, due to the temperature-dependence of packing factor and deviations from fluidity-free space proportionality, the equation can be used only within small temperature ranges.

In the hole theory of liquids, a liquid is assumed to be composed of a random distribution of molecules separated and surrounded by free space in between them, which is divided into a large number of smaller units, known as holes. These holes are supposed to be moving within the bulk of the liquid. Most of the physical properties of liquids can be explained with the help of this picture. The flow of a liquid is considered to be the jump of molecules from one hole into another by the action of some shearing stress, and hence, may be regarded as dependent on the number of such holes in a given quantity of liquid.

Free Volume

From this geometrical picture it can be easily shown that the free volume, V_f, in a liquid (*i. e.* the volume of a hole) is related to the liquid volume, V, as

$$V_f = C^3 (V^{1/3} - d)^3 \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where C is the packing factor, its value being 2 in the case of cubical packing in a liquid and may change with temperature, and d is the molecular diameter. Differentiating equation (1) with respect to V, and from the consideration of partition function of a molecule in the liquid and Helmholtz free energy expression, it was shown by Eyring *et al.* (*J. Phys. Chem.*, 1937, **41**, 219; Glasstone, Laidler and Eyring, "The Theory of Rate Processes", Mc Graw-Hill, New York, 1941, p. 479) that

$$p + \frac{\Delta E_{vap.}}{V} = \frac{CRT}{V^{2/3} . V_f^{1/3}}$$

(where $\Delta E_{vap.}$ is the energy of vaporisation per mol. $= L - RT$, L being the normal latent heat of vaporisation). The pressure, p, can be neglected in comparison with the second term of the equation. Hence for the free volume, we get

$$V_f^{1/3} = \frac{CRT . V^{1/3}}{\Delta E_{vap.}}.$$

If V_f represents the total free volume in a gram-molecule of liquid, then

$$V_f = \frac{C^3R^3T^3}{(\Delta E_{vap.})^3} \cdot V \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where V represents the molar volume.

Free Volume and Viscosity

It is interesting to note that the temperature coefficient of viscosity of non-associated liquids at high pressure is negligibly small at constant volume. This shows that viscosity is not independent of liquid volume or, more reasonably, the free volume. As it has already been pointed out that a hole is necessary for a liquid to flow, qualitatively it may be assumed that its fluidity (reciprocal of viscosity) is proportional to the number of holes. If η represents the viscosity of a liquid at temperature t and V_f, its free volume at the same temperature, then they are assumed to be related (Hatschek, "The Viscosity of Liquids," G. Bell, London, 1928, p. 70) as:

$$\eta V_f^a = \text{constant} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where a is some constant. Now, Eyring and Kincaid (*J. Chem. Phys.*, 1938, **6**, 620) have derived the following relation between free volume and velocity of a longitudinal wave (U) in a liquid:

$$U = \left(\frac{V}{V_f}\right)^{1/3} \sqrt{\frac{\overline{RT\gamma}}{M}} \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

instead of the usual equation

$$U = \sqrt{\frac{\overline{RT\gamma}}{M}}$$

for gases. Eliminating V_f between equations (3) and (4) Mukherjee (this *Journal*, 1951, **28**, 363) obtained a relation between U and η of the form

$$\log U = \log B + \frac{1}{2}\log T + \frac{1}{3a}\log \eta - \frac{1}{3}\log \rho \quad \ldots \quad \ldots \quad (5)$$

where B is a constant and ρ is the density of the liquid. Examining equation (5) with the aid of experimental data on velocity of sound in liquids (Lagemann *et al.*, *J. Chem. Phys.*, 1949, **17**, 369; 1948, **16**, 247; Pellane and Galt, *ibid.* 1946, **14**, 608) Mukherjee (*loc. cit.*) has established that for most non-associated liquids a is very near to unity. Hence equation (3) may be written as

$$\eta = \frac{k}{V_f} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3')$$

k being constant.

Viscosity and Temperature

Combining equations (2) and (3') one gets

$$\eta = \frac{A(\Delta E_{vap.})^3}{T^3 V} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

As a first approximation the packing factor, C, has been taken to be a constant as has also been done by Glasstone *et al.* (*loc. cit.*, p. 485) and by Kampfmeyer (*J. Appl. Phys.*, 1952, **23**, 99) in the calculation of activation energy.

In equation (6) V is a function of temperature. The coefficient of expansion in volume of a liquid can be defined by the expression :

$$\alpha = \frac{1}{V}\left(\frac{dV}{dt}\right)_P$$

Assuming α to remain constant, we have on integration

$$V = B\, e^{\alpha t} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

Substituting for $\Delta E_{vap.}$ we get from equations (6) and (7) the following relation between η and t.

$$\eta = K\left(\frac{L}{t+273.2} - R\right)^3 e^{-\alpha t} \quad \ldots \quad \ldots \quad (8)$$

For more accurate representation of the phenomenon we must take into account the variation of L with T and the inadequacy of the assumption of α to be constant. For many substances the variation of L with T may be represented (Saha and Srivastava, "A Treatise on Heat," Indian Press, Allahabad, 1950, p. 472) by

$$L = L_0 - aT$$

and the thermal expansion of a liquid is generally expressed by a polynomial of the type

$$V = V_0\,(1 + at + bt^2 + ct^3).$$

Substituting these expressions in (6) and (7) we get

$$\eta = \frac{K'\left(\frac{L_0}{t+273.2} - B\right)^3}{(1+at+bt^2+ct^3)} \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

where K is a new constant and B, a constant different from the gas constant R.

As equations (8) and (9) are cumbersome and are difficult to be tested with experimental data, these have been simplified so as to test them experimentally.

Comparison with Experimental Data

Since the variation of the volume of a liquid with temperature is small compared to its viscosity variation, one may neglect the former. Hence, from equation (9) we have

$$\eta = \left(A + \frac{B}{T}\right)^3 \quad \ldots \quad \ldots \quad \ldots \quad (10$$

i.e. a plot of $\eta^{1/3}$ against $1/T$ should yield a straight line. This is actually the case with such non-associated liquids as $CHCl_3$, C_8H_{18}, C_7H_{16}, C_6H_{14} and C_5H_{12} between 0° and their boiling points. Table I records the values of η calculated by equation (10) along with its observed values for *n*-hexane. Considering the nature of the approximations involved, the agreement is very good. For a number of liquids A is very small as compared with the other term of the equation (10), and thus, it accounts for Batschinski's empirical formula (*Bull. Soc. Natur. Moscow*, 1901, **15**, 1)

$$\eta = \frac{C}{T^3}.$$

TABLE I

n-Hexane.

$A = 0.0025$. $B = 42.48$.

$t°$.	$\eta \times 10^4$ (pois)		$\frac{\eta_c - \eta_o}{\eta_o} \times 10^2$.	$t°$.	$\eta \times 10^4$ (pois)		$\frac{\eta_c - \eta_o}{\eta_o} \times 10^2$.
	Obs.	Calc.			Obs.	Calc.	
0°	39.71	39.54	−0.42	36.76°	27.22	27.20	−0.07
9.15°	35.81	35.85	+0.11	43.47°	28.57	25 55	−0.08
14.75°	33.78	33.86	+0.24	47.42°	24.70	24.65	−0.20
19.98°	32.02	32.09	+0.22	52.90°	23.51	23.42	−0.38
25.39°	30.35	30.38	+0.09	58.76°	22.31	22.21	−0.44
30.23°	28.94	29.00	+0 21	63.59°	21.43	21.43	0

For a large temperature range V should not be taken constant. As a first approximation its variation with temperature may be taken to be represented by

$$V = a + bT.$$

Then equation (6) may be written as

$$\eta = \left\{ \left(A + \frac{B}{T} \right) \left(a + bT \right)^{-\frac{1}{3}} \right\}^3$$

and since b is a very small quantity, the above equation becomes

$$\eta = \left(A + \frac{B}{T} + CT \right)^3 \qquad \ldots \qquad \ldots \quad (11)$$

This equation is applicable to many non-associated liquids over wide ranges of temperature. For mercury (Table IIA) the agreement between the observed and the calculated values of η is excellent. In the case of gallium (Table IIB) the agreement is also good considering the wide temperature range.

TABLE II

A. *Mercury.*

$A = 0.12193$. $B = 32.65$. $C = 0.00005339$.

$t°$.	$\eta \times 10^4$ (pois)		$\frac{\eta_c - \eta_o}{\eta_o} \times 10^2$.
	Obs.	Calc.	
−20°	185	184.9	−0.05
0°	168	168.0	0
20°	155	154.4	−0.39
50°	139	138 7	−0.21
100°	121	120.7	−0.25
150°	109	109.0	0
200°	101	101.1	+0.10
250°	96	95.65	−0.36
300°	92	92.00	0
350°	90	89.52	−0.53

B. *Gallium.*

$A = 0.161784$. $B = 34.53$. $C = -0.00000602$.

$t°$.	$\eta \times 10^4$ (pois)		$\frac{\eta_c - \eta_o}{\eta_o} \times 10^2$.
	Obs.	Calc.	
52.9°	189.4	187.5	−1.0
102°	160.4	159.3	−0.68
149°	140.6	140.1	−0.35
200°	125.8	124.7	−0.87
301°	102.9	104.3	+1.3
402°	88.20	91.18	+3.4
500°	81.27	81.66	+0 48
600°	76.37	75 43	−1.2
806°	65.24	65.69	+0.69
1010°	59.15	59.27	+0.20
1100°	57.83	57.05	−1.3

Equation (11) can be applied to associated liquids only over small temperature ranges because of the approximations involved in it. Firstly, for these liquids fluidity is not strictly proportional to the free volume but to some power of it and consequently η should actually be equal to some power other than 3 of the expression

$$\left(A + \frac{B}{T} + CT \right).$$

Secondly, in these liquid the packing factor may vary considerably with temperature due to the dependence of association on the latter quantity. Table III records the observed values of η along with those calculated from equation (11) over a temperature range of 0°-60° for methyl alcohol.

TABLE III

Methyl alcohol.

$A = -0.3216$. $B = 112.1$. $C = 0.0004103$.

	$\eta = 10^4$ (pois)				$\eta \times 20^4$ (pois)		
$t°$.	Obs.	Calc.	$\frac{\eta_c - \eta_o}{\eta} \times 10^2$.	$t°$.	Obs.	Calc.	$\frac{\eta_c - \eta_o}{\eta_o} \times 10^2$.
0°	81.3	81.21	−0 11	40°	45.0	44.92	−0.17
10°	68.6	69.23	+0.91	50°	39.6	39.38	−0.55
20°	59.1	59.39	+0.49	60°	34.9	34.91	+0.03
30°	51.5	51.47	−0.06				

All the data have been taken from the International Critical Tables save those for gallium which have been taken from Spell's data (*Proc. Phys. Soc.*, 1936, **48**, 299).

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BORON TRIFLUORIDE AS A NEW CONDENSING AGENT IN THE PECHMANN REACTION

By (Mrs.) L. G. Shah, G. D. Shah and R. C. Shah

Resorcinol, methyl β-resorcylate, β-resorcylic acid and resacetophenone have been condensed with ethyl acetoacetate in presence of boron trifluoride-ether complex when 7-hydroxycoumarin derivatives were obtained in the first three cases. Condensation of methyl β-resorcylate and resacetophenone with ethyl acetoacetate in presence of gaseous boron trifluoride yielded mainly 5-hydroxycoumarin derivatives.

Numerous condensing agents have been used in Pechmann condensation (Roger Adams, "Organic Reactions", Vol. VII, p. 1). Sethana, Shah and Shah (*J. Chem. Soc.*, 1938, 228) used anhydrous aluminium chloride, dissolved in dry ether or dry nitrobenzene, in the condensation of β-ketonic esters with resorcinol, methyl β-resorcylate and β-resorcylic acid, and obtained mainly or exclusively 5-hydroxycoumarin derivatives instead of 7-hydroxy coumarin derivatives, which are usually obtained when concentrated sulphuric acid is used as a condensing agent. This behaviour has been attributed to the existence of chelation (Baker *et al.*, *J. Chem. Soc.*, 1935, 628; Thakor, *Curr. Sci.*, 1953, **22**, 117; Sethna *et al.*, *loc. cit.*). In the light of these findings it was thought interesting to study boron trifluoride-ether complex and boron trifluoride gas as condensing agents in the Pechmann reaction.

Ethyl acetoacetate in presence of boron trifluoride-ether complex under conditions as detailed in the experimental, condensed with (*i*) resorcinol, (*ii*) methyl β-resorcylate and (*iii*) β-resorcylic acid, furnishing 7-hydroxycoumarin derivatives. No trace of 5-hydroxycoumarin derivatives could be isolated from the above reactions. Resacetophenone failed to condense with ethyl acetoacetate, the reactants being recovered unchanged.

Methyl β-resorcylate and ethyl acetoacetate in nitrobenzene, using boron trifluoride gas at 0°-5°, yielded a mixture of methyl-5- and-7-hydroxy-4-methylcoumarin-6-carboxylates. Resacetophenone under similar conditions yielded 4-methyl-5-hydroxy-6-acetylcoumarin.

Though the yields of coumarin derivatives are poor, it is interesting to note here that boron trifluoride gas and boron trifluoride-ether complex have different condensing properties in this reaction. Boron trifluoride-ether complex like sulphuric acid gives 7-hydroxycoumarin derivatives, whereas boron trifluoride gas and anhydrous aluminium chloride have similar condensing properties, both yielding a mixture of 5- and 7-hydroxycoumarin derivatives.

These observations are of significance as they may help to elucidate the mechanism of β- and γ-substitution in the resorcinol nucleus under different condensing agents.

EXPERIMENTAL

Condensation of Resorcinol with Ethyl Acetoacetate in presence of Boron Trifluoride-ether Complex

Resorcinol (5.5 g., 1 *M*) and ethyl acetoacetate (6.6 g., 1 *M*) were dissolved in dry ether (20 c.c.) and boron trifluoride-ether complex (14 g., 2 *M*) was added slowly with cooling and shaking. The reaction mixture was then kept overnight when some crystals of m.p. 170°-180° separated. These were filtered and the filtrate was poured in cold water when a pasty mass separated which solidified on keeping. The above compound (m.p. 170°-180°) was crystallised from alcohol when colorless needles of 7-hydroxy-4-methylcoumarin (m.p. 185-86°) were obtained (m.p. 185°, Pechmann and Duisberg, *Ber.*, 1883, **16**, 2122). (Found : C, 68.3 ; H, 4.7. Calc. for $C_{10}H_8O_3$: C, 68.1 ; H, 4.7 per cent). The substance, obtained on pouring the reaction mixture into water, on crystallisation from alcohol yielded a further quantity of 7-hydroxy-4-methylcoumarin ; total yield 4.5 g.

Condensation of Methyl β-Resorcylate with Ethyl Acetoacetate

(*a*) *Using Boron Trifluoride-ether Complex.*—A mixture of methyl β-resorcylate (4.2 g.) and ethyl acetoacetate (3.2 g.) in boron trifluoride-ether complex (7. g.) was heated in a steam-bath for 2 hours and then the reaction mixture was poured on ice. The paste obtained was washed with cold water and then with sodium bicarbonate solution. It was then crystallised several times from alcohol when pure colorless needles of methyl 7-hydroxy-4-methylcoumarin-6-carboxylate separated, yield 0.7 g., m.p. 212-14° (m.p. 212-14°, Sethana *et al.*, *loc. cit.*). Mixed m.p. with an authentic sample was undepressed.

The same result was obtained when the above reaction was carried out in dry nitrobenzene as a solvent, other conditions remaining the same.

(*b*) *Using Boron Trifluoride Gas.*—Ethyl acetoacetate (9.7 g., 1 *M*) and methyl β-resorcylate (12.8 g., 1*M*) were dissolved in dry nitrobenzene (100 c.c.) and cooled to 0°-5. Boron trifluoride gas was then passed into it till saturation (about ½ hour), and kept overnight at room temperature. It was then heated at 70°-80° for 2 hours, cooled and poured in water. Nitrobenzene was then removed by steam distillation. The residual brown solid was fractionally crystallised from rectified spirit. Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate, m. p. 185-87°, yield 1.4 g. (m.p. 185-86°, Sethna *at al.*, *loc. cit.*) and methyl 7-hydroxy-4-methylcoumarin-6-carboxylate, m. p. 212-14°, yield 0.6 g. (m.p. 212-14°, Sethna *et al.*, *loc. cit.*) were obtained. Mixed m.p. of these compounds with authentic samples were undepressed.

Condensation of β-Resorcylic Acid with Ethyl Acetoacetate using Boron Trifluoride-ether Complex.—β-Resorcylic acid (3.8 g.), ethyl acetoacetate (3.25 g.) and boron trifluoride-ether complex (7.0 g.) were heated in a steam-bath for 2 hours. On working up as in the case of methyl β-resorcylate, 7-hydroxy-4-methylcoumarin-6-carboxylic acid was obtained in colorless needles from alcohol, m.p. 283-85°, yield 0.2 g. (m.p. 284-85°, Sethna *et al.*, this *Journal*, 1937, **14**, 717). (Found : C, 60.4 ; H, 3.6. Calc. for $C_{11}H_8O_5$: C, 60.0 ; H, 3.6 per cent).

Condensation of Resacetophenone with Ethyl Acetoacetate

(*a*) *Using Boron Trifluoride-ether Complex.*—Resacetophenone (5.1 g.), ethyl acetoacetate (4.3 g.) and boron trifluoride-ether complex (10 g.) were heated in a steam-bath for about 2 hours and the reaction mixture was worked up as usual. Resacetophenone was recovered unchanged. The condensation did not take place also when nitrobenzene was used as a solvent in the above reaction.

(*b*) *Using Boron Trifluoride Gas.*—The condensation of resacetophenone (10.2 g.) with ethyl acetoacetate (8.7 g.) in dry nitrobenzene (130 c.c.) by passing boron trifluoride gas at 0-5° till saturated was carried out in the same way as in the case of methyl β-resorcylate. On working up as usual, 5-hydroxy-6-acetyl-4-methylcoumarin was obtained in colorless needles from alcohol, m.p. 164-65°, yield 0.4 g. (m.p. 164-65°, Sethna *et al.*, *loc. cit.*). Its mixed m.p. with an authentic specimen was undepressed.

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IODIMETRIC DETERMINATION OF ELEMENTARY RED PHOSPHORUS

By G. S. Deshmukh and M. Venugopalan

The quantitative aspect of the $P-I_2$ reaction has been investigated involving the oxidation of red phosphorus with iodine which proceeds to completion with the formation of certain specific oxidation products. Different solvents (KI, CCl_4 etc.) for iodine have been tried for the oxidative process, and it has been found that wherever an organic solvent is used, initial precipitation of phosphorus tri-iodide takes place, which is further hydrolysed slowly by the moisture present to phosphorus acid and HI. Whereas with I_2 in KI solutions, direct oxidation of P to a mixture of phosphorus acids, iodine being reduced to HI, has been observed.

Rupp (*Arch. Pharm.*, 1903, **241**, 321) and Viebock (*ibid.*, 1934, **272**, 88) have shown that solutions of iodine in KI or organic solvents can be used as fairly good oxidising agents for elementary phosphorus. They have inferred the formation of phosphorus acids, since the P^{III} compounds, being normally stable to iodine, are considered to be produced in labile forms. Deshmukh and Venugopalan (this *Journal*, 1953, **30** 747) observed that the difference in the quantity of iodine added initially to a given weight of phosphorus and that left over after its complete disappearance, *i.e.* the titre value at infinite time, served as a measure of the quantity of iodine required for the oxidation reaction. The present work was undertaken to investigate the factors affecting this reaction and to determine its applicability in the quantitative determination of elementary red phosphorus.

Experimental

Red phosphorus of B.D.H. laboratory reagent grade quality was purified by Buehrer and Schupp's method (*J. Amer. Chem. Soc.*, 1927, **49**, 9) and subsequently by the copper phosphide process (Deshmukh and Sant, *Anal. Chem.*, 1952, **24**, 901). Its purity was checked by the magnesium pyrophosphate procedure.

(*a*). A standard solution of iodine (12.7 g.) in KI (15-20 g.) was prepared and made up to a litre and checked with standardised thiosulphate against dichromate. Exactly $N/10$ arsenious oxide solution was prepared in pure sodium hydroxide.

Red phosphorus (0.01 – 0.08 g.) was taken in a clean dry Erlenmeyer flask and to it a known volume of the iodine in KI was pipetted, followed by 2-3 g. of pulverised B.D.H. sodium bicarbonate. The contents were swirled from time to time and kept aside for about 24 to 30 hours. When all the red P had been dissolved, *i.e.* when the oxidation was complete, the remaining solution of iodine was titrated against (*i*) standard thiosulphate with starch as an indicator or (*ii*) with arsenious oxide solution using sodium bicarbonate or a borax-boric acid buffer (4 g. of boric acid and 8 g of borax in 100 c.c. of water). In case of (*ii*) about 50-100 c.c. of this buffer solution was added and titrated against standard arsenious oxide, the end-point being noted by the disappearance of

blue colour with starch as an indicator It was observed that complete oxidation took place under the above experimental conditions when the molar ratio of P : I was 1:4 (Deshmukh and Venugopalan, *loc.cit.*). Tables I and II record typical sets of results.

TABLE I

Using standard $N/10$-sodium thiosulphate solution.

Red P taken	$N/10$-I_2 in KI added.	P calc. from re : I_2.	Diff.	Red P taken.	$N/10$-I_2 in KI added.	P calc. from re : I_2.	Diff.
0.0065 g.	50 c.c.	0.0065 g	0.0	0.0337 g.	75 c.c.	0.0334 g	−0 0003
0 0129	,,	0.0130	+0.0001	0.0354	,,	0.0351	−0.0003
0.0183	,,	0.0183	0.0	0.0386	,,	0.0383	−0.0003
0.0168	,,	0.0167	−0.0001	0.0436	,,	0.0432	−0.0004
0.0216	,,	0.0215	−0.0001	0.0567	100	0.0562	−0.0005
0.0283	,,	0.0281	−0.0002	0.0642	,,	0 0637	−0.0005
				0.0791	125	0.0783	−0.0008

TABLE II

Using standard $N/10$ arsenious oxide solution.

Red P taken	$N/10$-I_2 in KI added.	P calc from re : I_2.	Diff.	Red P taken.	$N/10$-I_2 in KI added.	P calc from re : I_2	Diff.
0.0088 g.	50 c.c.	0 00888	0.0	0.0334 g.	50 c c.	0.0332	−0.0002
0.0130	,,	0.0129	−0.0001	0.0342	75	0 0339	−0.0003
0.0210	,,	0 0209	−0 0001	0.0422	,,	0.0418	−0.0004
0.0226	,,	0.0225	−0.0001	0.0548	,,	0.0542	−0.0006

From the data the formation of both phosphorus and phosphoric acid may be inferred according to the reaction :

$$2P + 4I_2 + 7H_2O \longrightarrow H_3PO_4 + H_3PO_3 + 8HI.$$

Incidentally this supports the observation of Rupp (*loc.cit.*) and Viebock (*loc.cit.*).

(*b*). A solution of iodine in CCl_4 was prepared and preliminary standardisation with standard sodium thiosulphate carried out.

A known quantity of red phosphorus was weighed into an Erlenmeyer flask and 25 to 50 c.c. of iodine in CCl_4 was pipetted into it, followed by about 2 to 3 g. of pure pulverised B. D. H. $NaHCO_3$. It was kept aside for about 30 hours with frequent shaking. A red precipitate of phosphorus tri-iodide was formed. The contents were diluted with water when PI_3 hydrolysed to H_3PO_3 and HI, the HI being immediately neutralised by sodium bicarbonate at its initial stage of formation. The remaining excess iodine in CCl_4 layer was titrated at once with standard thiosulphate using starch as an indicator.

The above reaction was studied at higher temperatures. In this case a known weight of red P was weighed into a Kjeldhal type flask provided with a glass seal and a Liebig condenser along with 50 c.c. of iodine in CCl_4 and 3 to 5 g. of $NaHCO_3$. The condenser was fitted in and the whole system refluxed at about 60°-65° in a water-bath for about 10 hours. When all the phosphorus disappeared, the system was cooled slowly and the excess of iodine was titrated against standard thiosulphate.

For the titration relatioship, the formation of PI_3 showed that the molar ratio of P:I was 1:3 for I_2 in organic solvents (Viebock, *loc.cit.*). Table III shows a set of results at ordinary temperature. Table IV shows the results at higher temperatures (60°-65°).

TABLE III

Red P taken.	I_2 in CCl_4 added.	* P calc.	Diff.	Red P taken	I_2 in CCl_4 added.	* P calc.	Diff.
0.0088 g.	25 c.c.	0.0087 g	−0.0001	0.0258 g	50 c c.	0.0256 g	−0.0002
0.0115	,,	0.0114	−0.0001	0 0288	,,	0.0286	−0.0002
0.0177	50	0.0176	−0.0001	0.0329	,,	0.0326	−0.0003
0.0122	,,	0.0122	0.0	0.0384	,,	0.0380	−0.0004
0.0216	,,	0.0215	−0.0001	0 0446	,,	0.0441	−0 0005

* From re : I_2.

TABLE IV

Vol. of I_2 in CCl_4 added = 50 c.c.

Red P taken.	* P calc	Diff.	Red P taken.	* P calc.	Diff.
0.0062 g.	0.0062 g	0.0	0.0240 g	0.0238 g	−0.0002
0.0123	0.0123	0.0	0.0284	0.0282	−0.0002
0.0133	0.0132	−0.0001	0.0326	0.0324	−0.0002
0.0206	0.0205	−0.0001	0.0407	0.0403	−0.0004

* From reagent : iodine.

From the data the initial precipitation of PI_3 and its further slow hydrolysis to phosphorous acid and HI may be inferred according to the equation :

$$2P + 3I_2 + 6H_2O \longrightarrow 2H_3PO_3 + 6HI.$$

Treatment of the reaction product with water, immediately after the reaction, leads to the complete hydrolysis of PI_3 with the formation of phosphorus acid and HI. The results are in agreement with the observations of Viebock and Rupp (*loc.cit.*).

The use of excess sodium bicarbonate in the above reaction is to annul or neutralise the acidity, *i.e.*, to neutralise the HI formed in the reaction, for it has been observed that I_2 in acid solution is a weaker oxidising agent than I_2 in neutral or alkaline solutions. It is therfore likely that in acid medium the reaction may be retarded considerably. Presence of HI may also tend to reverse the reaction; the reaction may attain equilibrium and oxidation of phosphorus may be incomplete.

About 0.005 to 0.05 g. of red P can be estimated by the above procedure within limits of experimental error. The method yields accurate results with dry red phosphorus but with less pure and moist variety, the results have been found to be high, probably more of I_2 is being utilised by the adherent moisture present in P. The above method though time consuming, is simple and sufficiently accurate for routine work.

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VOLUMETRIC DETERMINATION OF RED PHOSPHORUS BY POTASSIUM PERIODATE

By G. S. Deshmukh and M. Venugopalan

The addition of acidified potassium periodate solution to red phosphorus leads to its gradual disappearance accompanied with the evolution of iodine. The present paper deals with the factors affecting this reaction and its utilisability in the determination of elementary phosphorus.

In continuation of earlier work on the oxidation of red phosphorus by potassium bromate, ceric sulphate and iodine (Deshmukh *et al.*, *Anal. Chem.*, 1952, **24**, 901; *Analyst*, 1951, **76**, 604; this *Journal*, 1953, **30**, 11, 747; this *issue*, p. 305) the utility of potassium periodate as a powerful oxidising agent has been studied. The above oxidant, when added to a suspension of phosphorus in acid medium, dissolves it gradually (Deshmukh and Venugopalan, *Proc. Indian Sci. Cong.*, 1953, Part III-A, Sec. 4, pp. 28, 282).

Potassium periodate in acid solution is a strong oxidising agent, reduction of which proceeds to free iodine according to the reaction :

$$2IO_4^- + 16H^+ + 14e = I_2 + 8H_2O \quad \ldots \quad \ldots \quad (i)$$

The iodine is oxidised by the periodate to positive univalent iodine as

$$3I_2 + IO_4^- + 8H^+ = 7I^+ + 4H_2O \quad \ldots \quad \ldots \quad (ii)$$

The end of the titration is reached through this reaction, completion of which is shown in the presence of a suitable indicator (starch) by the disappearance of the free iodine.

Numerous oxidation studies with potassium periodate led the above authors to investigate the possibility of using it for the oxidation of red phosphorus to phosphoric acid. Even though Bengeisser (*Annalen*, 1836, **17**, 254) has reported that periodic acid oxidises ordinary phosphorus to phosphoric acid, the available information in the literature about the quantitative oxidation of red phosphorus by KIO_4 is meagre.

Many quantitative oxidation processes involving the use of KIO_4 show that its oxidising property is almost equivalent to that of potassium iodate and bromate (Bottger, "Newer Methods of Volumetric Chemical Analysis," Chapman & Hall Ltd., London, pp-69—128, 1938). Moreover, KIO_4 is very stable (Rammelsberg, *Pogg. Ann.*, 1868, **134**, 320, 370; 1869, **137**, 308), even up to 300°, and it is observed that iodine has no action on a boiling solution of periodate (Philip, *ibid.*, 1869, **137**, 319).

The addition of acidified potassium periodate solution to red phosphorus leads to its gradual disappearance accompanied with the evolution of iodine. The present work was therefore undertaken to study the factors affecting this reaction and to determine its applicability to the determination of elementary phosphorus.

EXPERIMENTAL

Pure, dry red phosphorus (0.03 – 0.15 g.) was weighed into a Kjeldhal flask provided with a Liebig condenser attached with a ground glass seal. CCl_4 (10 c.c.) was added and an excess (10-12 times the weight of P taken) of pure B.D.H., A.R. quality potassium periodate was weighed into it. About 20 c.c. of $2N$-H_2SO_4 and 20 c.c. of water were then introduced, the condenser fitted in and the whole system refluxed for about 4 to 5 hours on a water-bath.

When the reaction was over, as shown by the disappearance of the red phosphorus, the flask was cooled gradually. The iodine, liberated during the oxidation process and retained in CCl_4 layer, was removed by blowing in a current of hot air.

The residual solution containing excess periodate was made up to 250 c.c. and 50 c.c. of this was titrated iodimetrically against standard thiosulphate.

The difference in the quantity of potassium periodate added initially to P and that left over after the completion of the reaction should correspond to the amount utilised in the oxidation of phosphorus.

Results show that five mols. of KIO_4 are equivalent to 7 mols. of phosphorus. A knowledge of the quantity of periodate utilised in the reaction is therefore useful for the direct determination of phosphorus. A typical set of results is shown in Table I.

TABLE I

Overall acidity : 0.5-2.0 N-H_2SO_4.

Red P taken.	KIO_4 taken.	KIO_4 Unreacted	KIO_4 Reacted	Red P calc.*	Diff.
0.0365 g.	0.3156 g.	0.1224 g.	0.1932 g.	0.0364 g.	0.0001
0.0410	0.5362	0.3195	0.2167	0 0409	0 0001
0.0438	0 4304	0.1989	0.2315	0.0435	0.0003
0.0448	0.4812	0.2442	0 2370	0.0447	0.0001
0.0470	0.4888	0.2402	0.2486	0.0469	0.0001
0.0490	0.4907	0.2306	0 2601	0.0491	0.0001
0.0592	0.5810	0.2673	0.3137	0.0592	0.0
0.0646	0.6311	0 2889	0 3422	0.0645	0.0001
0.0700	0.4251	0.0548	0.3703	0.0699	0.0001
0.0848	0.6756	0.2270	0 4486	0.0846	0.0002
0.0952	0.5926	0.0896	0.5030	0.0949	0.0003
0.1188	0.9367	0.3090	0.6277	0.1184	0.0004
0.1294	0.8665	0.1834	0 6831	0-1289	0.0005
0.1382	1.1468	0.4190	0.7278	0.1373	0 0009
0.1468	1.4502	0.6799	0.7703	0.1453	0.0015

* Calculated from reagent : KIO_4.

The agreement between the calculated and the weighed quantities of P proves the stoichiometry of the reaction.

The oxidation of P with potassium periodate may be represented according to the equations:

$$2KIO_4 \longrightarrow K_2O + I_2 + 7O \quad \ldots \quad \ldots \quad \ldots \quad (i)$$

$$2P + 5O \longrightarrow P_2O_5 \quad \ldots \quad \ldots \quad \ldots \quad (ii)$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad \ldots \quad \ldots \quad \ldots \quad (iii)$$

Combining the above equations, wet get

$$14P + 10KIO_4 + 5H_2SO_4 + 16H_2O \longrightarrow 5K_2SO_4 + 14H_3PO_4 + 5I_2 \quad (iv)$$

From equation (*iv*), it is observed that seven mols. of P are equivalent to 5 mols. of KIO_4.

The results in Table I show that the oxidation can be carried out to completion at an overall acidity of 0.5 to 2 *N*-H_2SO_4 within a reasonable experimental error of 1% for values of phosphorus ranging from 0.03 to 0.14. g approximately.

It was found essential to retain the iodine in the liberated state by means of CCl_4 until the oxidation was complete. After the reaction the iodine was blown out of the system.

The influence of acidity on the total reaction was studied by varying the concentration of the known volume of the acid added to the system from 0.5 to 5 *N* and also by refluxing red P only with aqueous KIO_4 solution. The results are recorded in Table II.

TABLE II

P taken.	KIO_4 taken.	KIO_4 Unreacted.	KIO_4 Reacted.	Overall acidity. (H_2SO_4)	P calc.	Diff.
0.0480 g.	0.4823 g.	0.2385 g.	0.2438 g.	0	0.0460 g.	−0.0020
0.0448	0.4812	0.2442	0.2370	0−1 *N*	0.0447	−0.0009
0.0470	0.4888	0.2402	0.2486	1−2	0.0469	−0.0001
0.0438	0.4304	0.1971	0.2333	2−3	0.0440	−0.0002
0.0457	0.3974	0.1488	0.2486	3−4	0.0470	0.0013
0.0446	0.448	0.0873	0.2575	4−5	0.0486	0.0040
0.0488	0.7327	0.4349	0.2978	>5 *N*	0.0562	0.0074

In a purely aqueous medium, the rate of reaction was found to be appreciably slow; a brisk evolution of iodine and rapid disappearance of phosphorus, however, occurred when the total acidity of the system was increased progressively above 2*N*.

The low results obtained in an aqueous medium may be attributed to the incomplete oxidation and subsequent conversion of P into phosphoric acid. It may be assumed that the low results invariably obtanied, when the solution is initially neutral, are due to the reduction of some of the iodine to iodide ion and not reacted upon by IO_4^- ion as due to insufficient acidity.

The high results, observed on exceeding the acid concentration from 2*N* to 5*N*, may be due to more of KIO_4 being consumed than is actually necessary to oxidise P according to the equation (*iv*). It is also likely that some of the periodate is decomposed by the high concentration of sulphuric acid present.

These results suggest therefore that acid concentration is an important determinant in the present method of estimation of P and that under the given experimental conditions (*vide supra*), it is possible to obtain quantitative results by maintaining the overall acidity of the system between 0.05 and 2 *N* sulphuric acid.

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REDUCTION OF POTASSIUM DICHROMATE BY POTASSIUM IODIDE IN PRESENCE OF SULPHURIC AND HYDROCHLORIC ACIDS

By B. P. Gyani and S. N. Prasad

The reduction of potassium dichromate by iodide ions in presence of increasing concentrations of H_2SO_4 and HCl has been extensively studied potentiometrically. The former leads to only one inflexion in the titration graph corresponding to 6 mols. KI per mol. of dichromate. $N/2$-HCl also furnishes the same results, but higher concentrations give two inflexions, one at 3 mols. potassium iodide and the other at 6 mols. The chloride ion also takes part in the reduction at these concentrations of HCl, and ICl appears to be formed before the first inflexion which gives back the chloride ions on further addition of KI. Considering the rate of reaction HCl should be preferred to H_2SO_4 and the concentration should be either $N/2$ or above 4 N. The inflexions are, however, much sharper in presence of sulphuric acid.

The value of potassium dichromate as a quantitative oxidising agent is well known. Hendrixon (*J. Amer. Chem. Soc.*, 1921, **43**, 14) appears to be the first to try this titration. Known amounts of 0.02 and 0.05N-$K_2Cr_2O_7$ were added to excess of acidified KI, and the unchanged iodide was titrated with standard $KMnO_4$. The dichromate showed its theoretical oxidising capacity by this method. Balwant Singh *et al.* (this *Journal*, 1937, **14**, 435 ; 1939, **16**, 95 ; 1940, **17**, 173) followed Hendrixon but used different solutions to determine the excess of KI. The above titrations are indirect. Hendrixon also carried out direct titration of iodide with dichromate (*J. Amer. Chem. Soc.*, 1921, **43**, 1309) and pointed out that concentration of H_2SO_4 should be at least 2 N, and found a long time to reach the true end-point. Hendrixon did not study the reaction in presence of HCl. Kolthoff (*Rec. trav. chim.*, 1920, **39**, 208) studied the above reaction both in HCl and H_2SO_4 and obtained accurate results within 0 to 0.4% in N-HCl.

It thus appears that the problem has not been fully investigated and a study of the reaction in higher concentrations of the acids is still wanting. All the previous workers concentrated their attention on the final end-point and no attempt had been made to ascertain the existence of other inflexions to explain the mechanism of reduction. The importance of potentiometric titrations in the elucidation of such stages is well known and the present work was undertaken with these ends in view.

Experimental

A.R. grade potassium iodide and potassium dichromate were used throughout these experiments. The iodide did not liberate iodine on acidification. The titrations were carried out in a three-necked Woulfe's bottle in which 100 c.c. of 0.005 M solution of potassium dichromate in different concentrations of H_2SO_4 ($N/2$, N, 2 N, 4 N and 6 N) and HCl ($N/2$, 2 N, 3 N, 4 N, 5 N, and 6 N) were taken. A bright platinum foil electrode (cleaned in chromic acid and glowed in an alcohol flame) was introduced through

the middle one so as to dip in the solution. A saturated calomel electrode was used as the other half element and connection was made with the help of agar-agar bridge; *N*-KI was added in small amounts from time to time and the mixture was vigorously shaken by hand after each addition. Enough time was allowed for equilibrium and the steady E.M.F.'s attained thereafter were read on a stretched wire potentiometer. The spot galvanometer used was sensitive enough to allow 0.5 mv. being read directly which was more than our requirement. The temperature of the cell was kept at 30° by immersing it in a constant temperature bath.

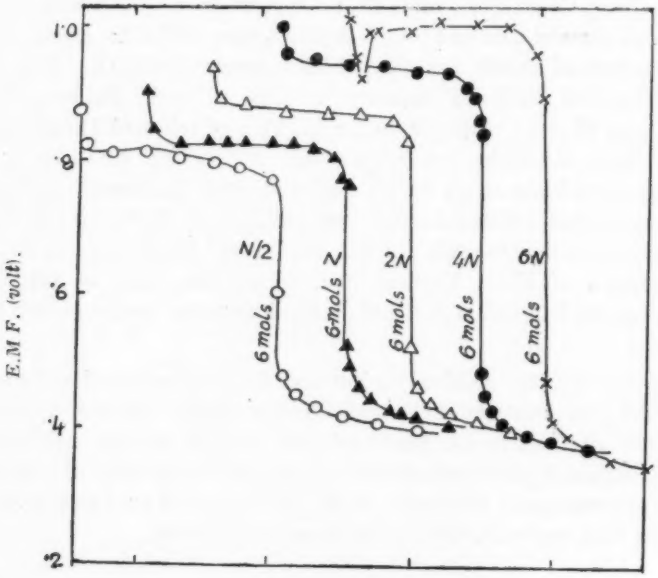
The results obtained in presence of H_2SO_4 are shown in Fig. 1. It will be found that all the curves are similar and the final inflexion is at $K_2Cr_2O_7 : KI = 1 : 6$. Iodine appeared right from the commencement of the titration and continued to be liberated till the end. The above ratio is simply explained on the basis,

$$K_2O.Cr_2O_3.3O + 6KI \rightarrow 4\ K_2O + 3\ I_2 + Cr_2O_3 \qquad \ldots\ (i)$$

The slight initial dip may signify presence of traces of reducible foreign impurities.

FIG. 1

Titration in presence of H_2SO_4.



Volume of KI *added.*

The titration graphs in presence of HCl (Fig 2) show two inflexions unless the acid concentration is low ($N/2$). The first of these occurs at three mols. of KI added per mol. $K_2Cr_2O_7$. This inflexion can by no means be due to conversion of potassium dichromate ($K_2O.Cr_2O_3.3O$) to potassium chromate ($2\ K_2O.Cr_2O_3.3O$, considering two molecules), since in this change no oxidation-reduction process is involved. As long as the first inflexion is not reached, the iodine liberated is redissolved on vigorous shaking,

and the yellow or green colour is restored, depending upon the progress of titration. At the first inflexion the colour is deep green, indicative of $CrCl_3$. At this stage therefore all the dichromate appears to have been reduced to Cr^{3+} which is strange when compared with the titration in presence of H_2SO_4. Only three electrons are available from 3 molecules of KI (*i.e.* from the three I^- ions) while the number required for total reduction is 6. The remaining 3 electrons must therefore come from Cl^-, the only other negatively charged ions in the solution, so that the essential reaction may be represented as

$$K_2O.Cr_2O_3.3O + 3\ KI + 3\ HCl \rightarrow 2\tfrac{1}{2}\ K_2O + 1\tfrac{1}{2}\ H_2O + 3\ ICl + Cr_2O_3 \quad \ldots\ (ii)$$

Further addition of KI introduces fresh iodide ions which can reduce the chlorine in ICl back to chloride ions,

$$3\ ICl + 3\ I^- \rightarrow 3\ I_2 + 3\ Cl^- \quad \ldots\ (iii)$$

The iodine should therefore be permanently liberated only after the first inflexion, if the above mechanism is correct. This was actually found to be the case. Further, 3 mols. of KI are required between the first and second inflexions, which is precisely what is required by reaction (*iii*). In other words, the chloride ions help the iodide ions to strip the dichromate ions of all available oxygen and are consumed in the process. To get back the chloride ions an equivalent quantity of iodide ions must be introduced.

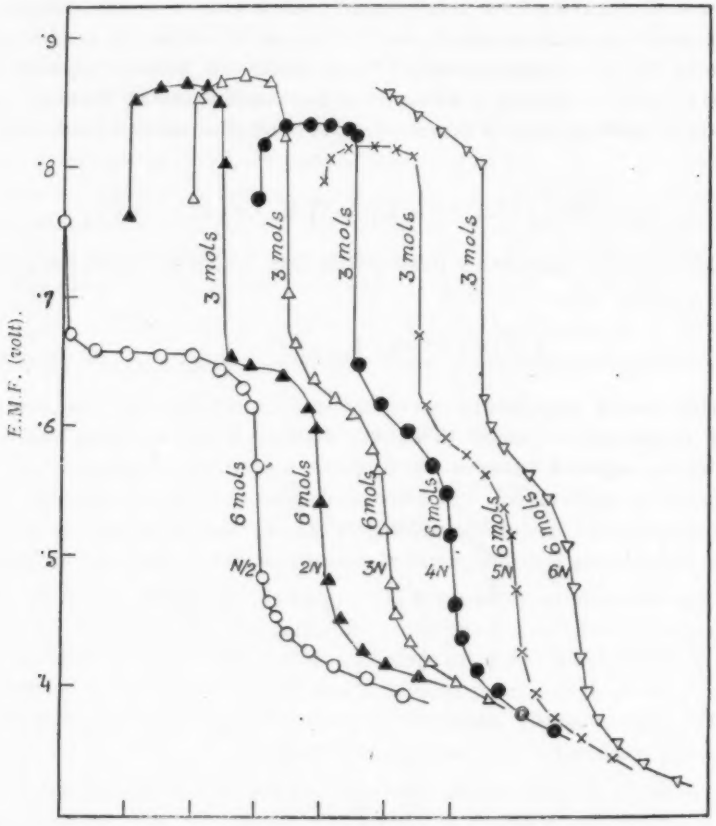
Since the reactions in presence of H_2SO_4 and HCl are quite different, one might naturally expect a difference in the rates. Reaction (*i*) appears to be a simpler one, and one may think that it might be quicker. It is fairly rapid in solutions of H_2SO_4 above normal, but is slow in lower concentrations, specially near the end-point. Concentration of H^+ ions obviously influences the rate although they do not enter reaction (*i*). The actual mechanism may therefore be different.

It was found in the other set of titrations that the rate of disappearance of iodine liberated before the first inflexion was larger, the greater the acid concentration. This is to be expected from reaction (*ii*). The rate was quite slow in 2 *N*-HCl but almost instantaneous in 6 *N*. The effect of increased concentration of HCl is therefore more easily understood in this titration. In *N*/2-HCl the chloride ions completely fail to bring about the reaction, so that the overall process is again represented by reaction (*i*).

To prove the presence of ICl 100 c.c. of *N*/2-$K_2Cr_2O_7$ in about 6 *N*-HCl was shaken with 25 c.c. of *N*-KI in a glass-stoppered bottle till the iodine that had first separated disappeared. It was then shaken with ether in a separating funnel. The ethereal layer was separated and shaken with water to remove the last traces of HCl. The ether was removed by boiling when a reddish liquid, smelling both of chlorine and iodine, was obtained. The properties of this substance are under investigation. Incidentally, Skrabal and Buchta (*Chem. Ztg.*, 1909, **33**, 1184) have shown that ICl is alone produced when iodine or an iodide is treated with a strong oxidising agent, when hydrochloric acid is also present.

FIG. 2

Titration in presence of HCl.



From the above investigations we conclude that for quicker titrations HCl should be preferred to H_2SO_4, and the concentration should be at least 4 N. For steeper inflexions H_2SO_4 has to be preferred (Fig. 2) and it is an advantage to have it at least 2N in the mixture. A titration in $N/2$-HCl is fairly accurate, economical and rapid.

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α-PICOLINE COMPLEXES OF SULPHATES OF ZINC, CADMIUM COBALT AND NICKEL

By G. C. Bhattacharya and P. C. Sinha

The following α-picoline complexes, $ZnSO_4$. 1 pico. $5H_2O$, $CdSO_4$. 2 pico. $2H_2O$, $CoSO_4$. 1pico. $2H_2O$ and $NiSO_4$.2pico, have been prepared by the interaction of sulphates of zinc, cadmium, cobalt and nickel respectively with α-picoline, and their properties described. Pressure-composition isothermals of the first two complexes have been determined and the remaining two do not decompose up to 100°. The heats of formation of the complexes have been determined by direct thermochemical methods by dissolving them in 6*N*-H_2SO_4. The stability of these complexes and influence of the basicity of the ligand on stability have been discussed.

When a metal ion combines with an electron donor, the resulting compound is called a complex or a co-ordination compound. The ligand, the co-ordination metal ion as well as the anion, all exert influence on the stability of the complex formed. The present work was undertaken with a view to determining the influence of the ligand on the stability of the complex. The co-ordination copmounds of the sulphates of Zn, Cd, Co and Ni with quinoline were described in previous papers (this *Journal*, 1950, **27**, 21, 30; 1953, **30**, 485). In the present paper, the composition and stabilities of the α-picoline complexes of the sulphates of the same metals are recorded. α-Picoline is chosen as a ligand as there is no mention in literature of the α-picoline complexes of the sulphates of these metals.

Experimental

As the sulphates of Zn, Cd, Co and Ni are insoluble in α-picoline, the method of preparation adopted is the same as that of the corresponding quinoline complexes (*loc. cit.*), namely, by adding gradually a saturated solution of the sulphate to a freshly distilled sample of α-picoline with constant stirring (1 to 3 hours' stirring was necessary for the formation of the complex). The crystals separated were collected, washed and dried.

All the complexes separated as shining crystals. While the zinc and the cadmium complexes are colorless, those of Co and Ni possess bright pink and light green colour respectively. The zinc complex is partially decomposed by water producing an opalescent solution due to the separation of zinc hydroxide. Complexes of Cd, Co and Ni are soluble in water and insoluble in alcohol, acetone and ether. Zinc, cobalt and nickel complexes are insoluble in benzene, but the cadmium complex is partially soluble in it.

For the estimation of α-picoline in the colorless complexes of zinc and cadmium, a measured volume of an excess of standard HCl was added to a weighed quantity of the complex. The substances dissolved in the acid and the excess of acid was titrated back with standard sodium hydroxide solution, using methyl orange as an indicator.

In the case of the coloured complexes of nickel and cobalt, α-picoline was steam-distilled into a measured volume of standard sulphuric acid and the excess of acid titrated back.

For determining the amounts of zinc and cadimium, the solutions left over after the titration of α-picoline were used. Zinc was precipitated as ammonium phosphate and weighed as pyrophosphate, and cadmium was precipitated as sulphide and weighed as sulphate. The nickel complex was stable in aqueous or weakly acid solution. It had to be boiled with HCl (conc.) and Ni was estimated as the dimethylglyoxime complex. Cobalt was estimated in the solution left in the flask after steam distillation of α-picoline by electrodepositing the metal on a platinum cathode. The sulphate was determined as barium sulphate. The results are recorded in Table I.

TABLE I

Complex	$ZnSO_4.1pico.5H_2O$.		$CdSO_4.2pico.2H_2O$.		$CoSO_4.1pico.2H_2O$.		$NiSO_4.2pico$.	
	Found.	Calc.	Found.	Calc.	Found	Calc.	Found.	Calc.
M	18.8%	18.9%	26 1%	26.1%	20.8%	20.8%	16.9%	17.2%
SO_4''	27.7	27.9	22.3	22.3	33.6	33.8	27 8	28.2
Pico.	28.1	27.0	41.9	43.2	32.4	32.7	54.6	54,6
H_2O (diff.)	25.4	25.2	9.7	8.4	13.2	12.7	...	...

M stands for the respective metal ion and the data under 'found' are mean of 3 readings.

The composition of the complexes has been established by analysis. It will be seen from Table I that except the Ni complex, all others contain water of crystallisation. The crystals are stable in air at the room temperature and they do not lose water up to 55°. The compound, $ZnSO_4.\ 1pic_0.\ 5H_2O$, loses 3 molecules of water when heated at 60°-65° for one hour. The remaining two molecules are firmly held and are not removed when heated to 100°; $ZnSO_4.$ 1pico. $2H_2O$ does not also decompose at that temperature. Between 60° and 65°, $CdSO_4.$ 2pico. $2H_2O$ loses one molecule of water in one hour and the whole of its water in 3 hours. On further heating, the dehydrated cadmium complex begins to lose α-picoline gradually until the whole of the ligand is lost. The partially dehydrated Zn complex readily takes up moisture from the air and is finally reconverted into the pentahydrate. The dehydrated cadmium complex, on the other hand, takes up mois ure with extreme slowness. The two molecules of water in the Co-complex are rigidly held, there being no loss when heated at 100° for 4 hours. The Ni-complex is also quite stable at 100°.

Pressure-composition Isothermals

The pressure-composition isothermals of α-picoline complexes of zinc and cadmium sulphates have been determined. The apparatus employed is practically the same as that described by Ray and Sinha (*Trans. Faraday Soc.*, 1948, **44**, 790) with a slight modification that in place of the inset shown in their diagram, the arrangement shown in Fig. 1. introduced. This modification prevents occasional leakage of mercury from the mercury-seal into the bulb containing the substance.

FIG. 1

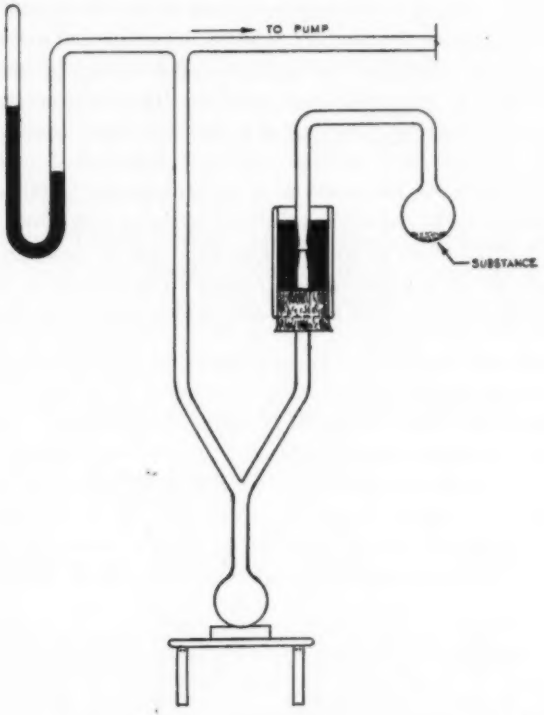


TABLE II

$ZnSO_4$. 1pico. $5H_2O$ at 60°.

Pressure (mm. of Hg).	Total wt. of water in successive stages.	No. of mols. of water in the bulb per atom of Zn.
20.2	0.1482	5.00
,,	0.1247	4.36
,,	0.0982	3.44
,,	0.0882	3.08
,,	0.0707	2.47
,,	0.0597	2.09
3.4	0.0517	1.89
,,	0.0445	1.55
,,	0.0389	1.36

TABLE III

$CdSO_4$ 2pico. $2H_2O$ at 60°.

Perssure (mm. of Hg.)	Total wt. of water in successive stages.	No. of mols. of water in the bulb per atom of Cd.
8.8	0.0474	2.00
,,	0.0426	1.80
,,	0.0380	1.61
,,	0.0328	1.39
,,	0.0286	1.21
4.4	0.0221	0.93
,,	0.0152	0.64
,,	0.0100	0.42
,,	0.0055	0.23

The results of pressure-composition measurements are recorded in Tables II and III. The isothermal curves are shown respectively in Figs. 2 and 3. It was not possible to determine the isothermals of α-picoline complexes of nickel and cobalt sulphates since their pressures even up to 100° were so low that they could not be measured with any degree of accuracy.

The stability of these complexes could not be determined by the dissociation perssure measurements. As these complexes contain water, the presence of two volatile constituents in the molecule of the complex renders the evaluation of pressure uncertain. The stability of these complexes has therefore been determined by measuring their heats of formation directly by thermochemical means. The calorimeter set up and the method adopted were the same as described in a previous paper (this *Journal*, 1950, **27**, 22). The heat of solution of α-picoline was first determined in a known volume of $6N$-H_2SO_4 and then the heat of solution of an accurately weighed quantity of the complex was measured using the same volume of the acid each time, making the usual corrections for the heating effect of stirring and the loss of heat by radiation. From these data the heat of formation of the complex was calculated by the application of Hess's law of heat summation. The results obtained are shown in Table IV.

TABLE IV

Av. value of the thermal capacity of the calorimeter = 158.1 cals./degree.

Complexes.	Wt.	Temp. rise (corr.)	Heat of reaction (cals. per G. F. W.)	Mean q_1 (cals.)	Heat of formation (cals. per G. F. W.).
$ZnSO_4$. 1pico. $5H_2O$	1.6370 g.	0.052°	1,725		
	1.6368	0.052°	1,720	1,765	8,295
	1.5923	0.054°	1,850		
$CdSO_4$.2pico. $2H_2O$	0.6941	0.115°	11,310		
	1.0021	0.168°	11,420	11,280	8,840
	0.9926	0.162°	11,111		
$CoSO_4$. 1pico. $2H_2O$	0.9720	0 040°	1,840		
	1.1249	0.048°	1,932	1,900	8,160
	1.1250	0.048°	1,928		
$NiSO_4$. 2pico.	0.6409	0.122°	10,260		
	0.8642	0.165°	10,320	10,267	9,853
	0.9211	0.175°	10,240		
α-Picoline	1.3921	0.950°	10,020	q_2.	
	0.9371	0.646°	10,160	10,060	...
	1.5296	0.960°	10,000		

The heat data recorded in Table IV represent the heats of formation of the complexes obtained by interaction of a saturated solution of the sulphate with α-picoline. The heats of formation of the α-picoline complexes with anhydrous sulphate can be calculated by the equation,

$$Q = q_3 + nq_2 - q_1$$

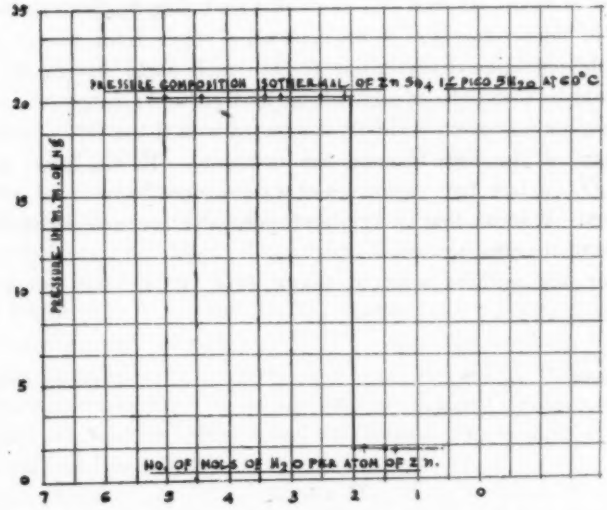
where Q stands for the heat of formation of the complex between the anhydrous sulphate and α-picoline, q_3 for the heat of solution of the anhydrous sulphate in $6N$-H_2SO_4, q_2 for the heat of neutralisation of α-picoline in the same acid, q_1 for the heat of reaction of the complex in the same acid, and n is the number of molecules of the ligand in the complex. Taking the values of q_3 for anhydrous zinc sulphate and cadmium sulphate to be 18,430 cals. and 10,740 cals. respectively (International Critical Tables), the heats

of formation of $ZnSO_4$. 1pico. $5H_2O$ and $CdSO_4$. 2pico. $2H_2O$ work out to be 19,580 cal./G.F.W. and 26,725 cal./G.F.W. respectively. The value for the corresponding nickel and cobalt complexes cannot be calculated as the value of q_3 for anhydrous nickel and cobalt sulphates are not available, and although pure perfectly dehydrated sulphates of nickel and cobalt were prepared, their solution in $6N$-H_2SO_4 was so slow that their heats of solution could not be determined accurately.

Discussion

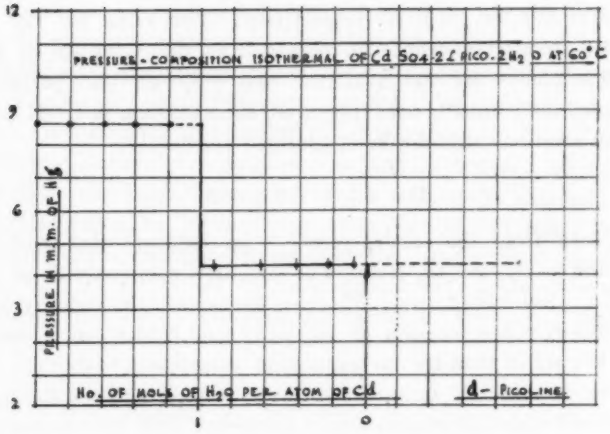
It will be seen from the results recorded in Table IV that the nickel α-picoline complex is the most stable, and the stability of the other complexes is in the following order. Cd, Zn, Co. Euler (*Ber.*, 1904, **37**, 2768) determined the stability of the metallic pyridine complexes by measurements of solubility and E.M.F. and found that pyridine complexes were less stable than the corresponding complexes containing ammonia and alkylamine. The decrease in stability may be connected with the strength of the base. If the stability of the α-picoline complexes are compared with the corresponding quinoline complexes, previously reported (*loc. cit.*), the quinoline complexes are found less stable than the corresponding α-picoline complexes. Quinoline is a weaker base than α-picoline, their heats of neutralisation per gram formula weights being 6,280 cals. and 10,060 cals. respectively. It would seem therefore that stronger the base, the stabler the complex formed, but it would not be safe to generalise from insufficient data.

Fig. 2



The isothermal curves of the complexes $ZnSO_4$. 1pico. $5H_2O$ and $CdSO_4$. 2pico. $2H_2O$, represented in Figs. 2 and 3 respectively, show only one break in each case, indicating the existence of two solid phases for each complex, namely, $ZnSO_4$. 1pico. $5H_2O$ and $ZnSO_4$. 1pico.$2H_2O$ in the case of the zinc complex and $CdSO_4$.2pico.$2H_2O$ and $CdSO_4$.2pico.H_2O for the cadmium complex. In the case of the latter complex,

FIG. 3



however, when the last molecule of water was removed the dehydrated α-picoline complex was left, but the manometer recorded only slight change of pressure which was too small to be measured. The α-picoline was gradually removed under suction showing practically no variation of pressure from the monohydrated complex. It appears therefore that although in Fig. 3 only one break is obtained, the complex is capable of existence in three solid phases, the last one being $CdSO_4.2$pico. From the point of view of energy changes, it may be said that each dehydration reaction corresponds to the severance of valence forces or to the removal of water from a well-defined lattice position against the operation of crystalline forces, each stage having its own heat of reaction. It would be seen that, as pointed out by Biltz and Grimm (*Z. anorg. Chem.*, 1925, **45**, 63), complex formation is closely connected with the nature of crystal lattice and the lattice energy of the salt, forming the complex. In the case of the complex $ZnSO_4.1$pico.$5H_2O$, the last two molecules of water cannot be removed without breaking down the complex. It seems that two molecules of water are neccessary for maintaining the crystal lattice of the complex ion.

In conclusion the authors wish to thank Prof. R. C. Ray for his kind interest and help.

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A NOTE ON COUMARINS DERIVED FROM *p*-ALKYLPHENOLS

By M. R. Bhatt and N. M. Shah

The present work was undertaken to synthesise the hitherto unknown coumarin derivatives from *o*- and *p*-alkylphenols under the conditions of the Pechmann reaction (Organic Reactions, Vol. VII, Chapter 1). It is noteworthy that *o*-alkylphenols do not undergo the Pechmann reaction.

p-Ethyl-, *p*-butyl- and *p*-benzyl-phenols condensed smoothly with ethyl acetoacetate as well as acetone dicarboxylic acid. The former yielded 4-methyl-6-alkylcoumarins (alkyl = Et, Bu, Bz), while the latter furnished the corresponding coumarin-4-acetic acids.

It is interesting to note that *p*-alkyl group in the phenol molecule is neither inhibitory nor retarding the Pechmann reaction, whereas the same group in *o*-alkylphenols inhibits the coumarin formation (Sethna and Shah, *Chem. Rev.*, 1945, **36**, 1).

6-Alkyl-4-methylcoumarins obtained from *p*-alkylphenols (3 g.) and acetoacetic ester (3.5 g.) under the usual conditions of the Pechmann reaction are recorded below. The coumarin obtained was crystallised from alcohol.

Table I

Alkyl=	Cryst. shape.	M.P.	Formula.	Analysis. Found.	Calc.
C_2H_5	Greyish tiny needles	69-70°	$C_{12}H_{12}O_2$	C : 76.4 % H : 6.3	76.6 % 6 5
C_4H_9	White tiny needles	59-60°	$C_{14}H_{16}O_2$	C : 77.6 H : 7.2	77.8 7.4
CH_2Ph	White needles	69°	$C_{17}H_{14}O_2$	C : 81.5 H : 5.3	81.6 5.6

Acetone dicarboxylic acid was condensed with the *p*-alkylphenols under the following general procedure to yield the corresponding 6-alkylcoumarin-4-acetic acids (Table II).

Powdered citric acid (8 g.) and H_2SO_4 (conc., 10 c.c.) were mixed and shaken for half an hour, and then heated at 65°-70°. After the frothing had subsided, the mixture was cooled in ice-bath, *p*-alkylphenol (3 g.) and H_2SO_4 (conc., 7-10 c.c.) added and the mixture left overnight. On treatment with crushed ice, the solid obtained was treated with $NaHCO_3$ solution, filtered and the filtrate was acidified, yielding the acid which was crystallised from alcohol.

Table II

Alkyl=	Cryst. shape.	M.P. (efferv.)	Formula.	Equiv. (titration). Found.	Calc.
C_2H_5	Small white needles	184-85°	$C_{13}H_{12}O_4$	231.5	232
C_4H_9	Flat needles	151-52°	$C_{15}H_{16}O_4$	258.4	260
CH_2Ph	Lustrous ,,	153-54°	$C_{18}H_{14}O_4$	295.1	296

The above coumarin-4-acetic acids on being decarboxylated by heating to their melting points furnished the corresponding alkylcoumarins, recorded in Table I. The coumarin-acids were esterified with $MeOH\text{-}H_2SO_4$ affording the methyl esters, as recorded below.

TABLE III

Esters.	Cryst. shape.	M.P.	Formula.	Found.	Calc.
Methyl 6-ethyl-coumarin-4-acetate	White fine needles	121-22°	$C_{14}H_{14}O_4$	C : 68.2 % H : 5.4	68.4 % 5.7
Methyl 6 butyl-coumarin-4-acetate	White needles	108-109°	$C_{16}H_{18}O_4$	C : 69.8 H : 6.5	70.1 6.6
Methyl 6-benzyl-coumarin-4-acetate	White needles	111-12°	$C_{19}H_{16}O_4$	C : 73.8 H : 4.9	74.0 5.2

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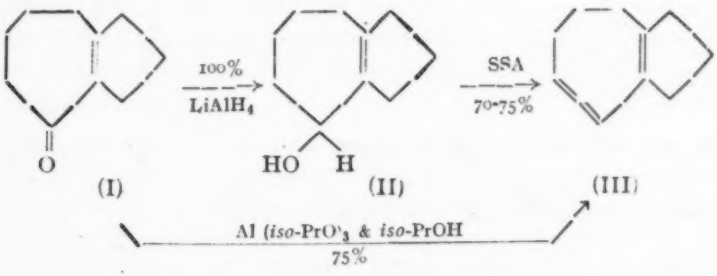
AZULENES AND RELATED SUBSTANCES. PART VII. DEHYDROGENATION OF AZULENE PRECURSORS

By Sukh Dev

Dehydrogenation of azulene precursors has been studied in the vapour phase under variations of temperature and contact time. It has thus been found possible to arrive at conditions which furnish azulene in 30% yield from 1:2:3:6:7:8-hexahydroazulene.

For a study of the interesting non-benzenoid quasi-aromatic hydrocarbon, azulene, it is essential that it should be readily accessible. With this end in view new methods have been developed for the preparation of *cyclo*penteno-*cyclo*heptanone (I) (Sukh Dev, this *Journal*, 1954, **31**, 1) and *cyclo*hepteno-*cyclo*pentanone (IV) (Sukh Dev, *ibid.*, 1955, **32**, 255) which serve as important intermediates in the preparation of azulene (Plattner and Pfau, *Helv. Chim. Acta*, 1937, **30**, 224; Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232). At the time, when the first phase of this work had been completed, the best procedure for the conversion of the ketone (I) into azulene was that of Anderson and Nelson (*loc. cit.*), but it suffered from the rather poor conversion (3.4%) of the hexahydroazulene (III) into the azulene in the final step of dehydrogenation. It was decided to investigate this phase of the synthesis in a detailed manner in order to arrive at optimum conditions for dehydrogenation.

1:2:3:6:7:8-*Hexahydroazulene* (III) was prepared essentially by the method of Anderson and Nelson (*loc. cit.*). These authors described the allylic alcohol (II) to be too unstable for analytical purposes. In fact, they reported that even at the temperature of its low melting point it readily underwent dehydration, and they carried out its conversion into the diene by the azeotropic distillation of its benzene solution without the aid of any catalyst.



In view of the well-known susceptibility of $\beta\gamma$-unsaturated alcohols to acid-catalysed dehydration (this is possibly due to the resonance stabilisation of the intermediate carbonium ion, as well as due to the lesser energy-content of the resulting conjugated diene), the working up of the $LiAlH_4$-reaction mixture was modified and the pure alcohol (II) was successfully isolated as a nicely crystalline compound of m.p. 57-58°; it *did not* dehydrate on melting. In fact, the m.p. of the resolidified melt

remained unaltered on repeating this operation ten times. However, the alcohol was quite labile and it started deteriorating after about a week at room temperature, and slowly passed into a syrup-like material (this behaviour was also observed under anhydrous condition). The decomposed mass furnished after purification a small amount of a dark red 2:4-dinitrophenylhydrazone, appearing to be identical with the derivative from the ketone (I). Though 2:4-dinitrophenylhydrazine in acidic-alcoholic solution (Braude *et al.*, *J. Chem. Soc.*, 1951, 1762; 1953, 2202) is known to effect the oxidation of certain allylic alcohols, the alcohol (II) under these conditions fails to yield the derivative corresponding to the ketone.

The dehydration of the alcohol was carried out in the presence of an acid-catalyst by a procedure described previously (Sukh Dev, this *Journal*, 1953, **30**, 789). Mere refluxing of its benzene solution did not produce the diene. The diene can also be obtained directly from the ketone on treatment with aluminium *iso*propoxide in *iso*propanol under the usual Meerwein-Ponndorf conditions. The hydrocarbon prepared by the acid-catalysed dehydration of the alcohol has three maxima at 250 mμ, 255 mμ and 260 mμ (cf. Anderson and Nelson *loc. cit.*); many dienes are known to exhibit three absorption peaks with one on either side of the principal band and almost equidistant from it (Dorfman, *Chem. Rev.*, 1953, **53**, 58). The position of the most intense band is what should be expected from the spectrum of *cyclo*heptadiene (λ_{max}, 248mμ; log ε, 3.87; Pesch and Friess, *J. Amer. Chem. Soc.*, 1950, **72**, 5756), when the expected bathochromic shift due to the alkyl substituents is taken into account. The conjugated diene was further characterised by the Diels-Alder condensation with maleic anhydride; the adduct on distillation with a little Pd-C readily furnished an azulene.

Since Anderson and Nelson (*loc. cit.*) claimed almost quantitative conversion of the alcohol into the diene, a preparation starting from the ketone (I) was carried out by following their details as closely as possible. Though a benzene solution of the crude alcohol was refluxed for several hours, only a trace of water separated, and we failed to isolate the diene in any appreciable yield by their procedure.

1:4:5:6:7:8-*Hexahydroazulene* (VI).—Lithium aluminium hydride reduction of *cyclo*hepteno-*cyclo*pentanone (IV), followed by dehydration of the resulting crude carbinol (V), furnished the desired *cyclo*pentadiene derivative (VI), which was characterised by the condensation with maleic anhydride (cf. Braude and Forbes, *J. Chem. Soc.*, 1953, 2208).

(IV) (V) (VI)

(VII) (VIII)

*Dehydrogenation Studies**

Günthard *et al.* (*Helv. Chim. Acta*, 1951, **34**, 959) carried out a systematic study of the dehydrogenation of 1:2:3:4:5:6:7:10-octahydroazulene and obtained a maximum of 11% yield of the azulene. Since the corresponding dienes should be more readily susceptible to dehydrogenation, a systematic study of this reaction on such precursors is expected to lead to a better method for the preparation of azulene. This has been realised to some extent (Table I).

It was anticipated that the controlling factors for dehydrogenation should be (*i*) the temperature of dehydrogenation, (*ii*) the contact time, as determined by the length of the catalyst bed and the time required for a given amount of the substance to pass through this, (*iii*) activity of the catalyst, and (*iv*) the purity of the material to be dehydrogenated.

TABLE I

Dehydrogenation of 1:2:3:6:7:8-*Hexahydroazulene.*

No.	Time.	Yield of the condensate.	Temp. (furnace).	Azulene in the condensate.	Yield of azulene.
1	10 hrs.	2.5 g.	300-305°	50 mg.	1.9 %
2	,,	2.5	320-325°	60	2.3
3	,,	2.5	355-360°	205	8.0
4	,,	2.4	375-380°	740	28.8
5	,,	2.2	400-410°	1000	38.0
6	½ hr.	2.6	,,	390	14 8
7	1	2.4	,,	500	19.0

It is clear from Table I that the formation of azulene from 1:2:3:6:7:8-hexahydroazulene (and using the conditions and set-up as detailed in the 'Experimental') reaches a maximum at *ca.* 400°-410° (furnace temperature); still higher temperatures have not been investigated as the rearrangement to naphthalene is expected to become serious (vide Heilbronner, Plattner and Wieland, *Exper.*, 1947, **3**, 70). The time of 10 hours (for passing 2.68 g. of the diene) was chosen arbitrarily; much lesser yields of azulene were obtained at 30 and 60 minutes' passage time. The purity of the diene was found to be of great importance, as even a slightly impure sample deactivated the catalyst.

Under these optimum (so far established) conditions, two other compounds were investigated for conversion into azulene. The isomeric diene, 1:4:5:6:7:8-hexahydroazulene (VI), gave a 30% yield of the azulene, while the mono-olefin, presumably (VII) (cf. Günthard *et al.*, *loc. cit.* But it is likely to be contaminated with $\Delta^{4(5)}$-and Δ^{8}-isomers; cf. Kovats, Fürst and Günthard, *Helv. Chim. Acta*, 1954, **37**, 534), under these conditions gave only 13.3% yield of the azulene.

* Since the completion of this work (Final Report to N.I.S.I., Sept. 1953), other workers have also described the conversion of various azulene precursors to azulene in 'good' yields (Prelog and Schenker, *Helv. Chim. Acta*, 1953, **36**, 1181; Anderson, Nelson and Tazuma, *J. Amer. Chem. Soc.*, 1953, **75**, 4980; Baker, Warburton and Breddy, *J. Chem. Soc.*, 1953, 4149; Kovats, Plattner and Günthard, *Helv. Chim. Acta*, 1954, **37**, 983).

Another variation, the effect of a diluent, was tried on the mono-olefin (VII). The olefin was dissolved in *p*-cymene and was passed through the catalyst bed under the above-established optimum conditions ; the yield of azulene dropped to 7.6%.

Azulene has been further characterised by the preparation of a complex with picramide (Dutt, Sukh Dev and Guha, this *Journal*, 1953, **30**, 473). Baker, Warburton and Breddy (*loc. cit.*, p. 4153) reported that azulene did not form a molecular compound with 2 : 4 : 7-trinitrofluorenone ; it had been possible to prepare the complex (black leaflets, m.p. 161-63°) from acetic acid solution, but the compound on attempted recrystallisation from the same solvent underwent decomposition to a black powder, which failed to regenerate any azulene.

The non-azulenic portion from the dehydrogenation experiments after purification can be recyclised. In the case of 1 : 2 : 3 : 6 : 7 : 8-hexahydroazulene, it was noticed that the recovered material had an appreciably lower refractive index ; however, its ultraviolet spectrum was practically identical with that of the pure diene (III). The fact that during dehydrogenation the diene undergoes considerable isomerisation to a thermodynamically more stable molecule, has been established by its reaction with maleic anhydride ; the recovered hydrocarbon furnishes a smaller yield of the adduct, and this after purification yields a small amount of the pure derivative, which has been identified with that derived from the isomeric diene (VI). It is suggested, however, that 1 : 4 : 5 : 6 : 7 : 8-hexahydroazulene (VI) is not the product of isomerisation, but is produced under the Diels-Alder reaction conditions (e.g., cf. the behaviour of β-phellandrene ; Goodway and West, *J. Chem. Soc.*, 1938, 2028) from the primary isomerisation product containing a more stable arrangement of double bonds (e.g. the heteroannular diene, VIII) ; this also appears to be supported by the fact that iodine-catalysed (iodine is a potent catalyst for the isomerisation of polyolefins) dehydration of Δ^9-octahydro-4-oxyazulene (II) furnishes a diene having a refractive index close to that of the recovered diene ; this product also shows the U.V. spectrum identical with that of the diene (III).

EXPERIMENTAL

All melting and boiling points are uncorrected. Petroleum ether refers to the fraction b.p. 40°-60°. The solvent extracts were dried over anhydrous sodium sulphate. The spectra were taken on a Beckman DU spectrophotometer.

Δ^9-*Octahydro-4-oxyazulene* (II).—To a fine slurry of lithium aluminium hydride (1.4 g., 0.037 *M*) in ether (75 c.c.) an ethereal solution of *cyclo*penteno-*cyclo*heptanone (15.0 g., 0.1 *M* ; in 30 c.c. + 10 c.c. of ether ; Sukh Dev, *loc. cit.*) was let in during five minutes with efficient stirring (Mag-mix) and cooling in an ice-salt-bath. The reaction mixture was stirred at the bath temperature for one hour and finally at room temperature for another 15 minutes. Excess of $LiAlH_4$ was decomposed by the cautious addition of ice-water (10 c.c.) and then treated with 10% H_2SO_4 (dilute, 75 c.c.) at below 0° to destroy the complex. The ether layer was removed and washed with water (50 c.c.) ; ammonium sulphate (100 g.) was dissolved in the aqueous portion, which was then extracted with ether (50 c.c. × 2). The combined ether extracts were washed with water (100 c.c. and finally with brine containing some $NaHCO_3$ (75 c.c. × 2). From the

dried solution the solvent was removed under slight vacuum from a bath held at 35°-40°, when a white crystalline residue (15.2 g., 100% ; m.p. 50-55°) of the alcohol was left; the material was used as such for the dehydration step. Two recrystallisations at 0° from dilute acetone furnished white, silky needles, m.p. 57-58°. (Found: C, 78.62 ; H, 10.62. $C_{10}H_{16}O$ requires C, 78.94 ; H, 10.52 per cent). Anderson and Nelson (*loc. cit.*) report m.p. 51-52° with loss of water.

A deteriorated sample (0.2 g., 2 months old) was treated with the 2 : 4-dinitrophenylhydrazine reagent (HCl method) ; a dark red product of m.p. 225°-230° (30 mg.) slowly separated. This on recrystallisation from benzene containing petroleum ether gave crimson, lustrous leaflets (10 mg.), m.p. 234-36° (decomp.) ; mixed m.p. with the 2 : 4-dinitrophenylhydrazone of ketone (1, m.p. 247-48°) was 237-39°. (Found : N, 17.5. $C_{16}H_{18}O_4N_4$ requires N, 17.0 per cent).

1 : 2 : 3 : 6 : 7 : 8-*Hexahydroazulene* (III)

(*a*). *By Meerwein-Ponndorf Reduction of the Unsaturated Ketone.*—A mixture of *cyclo*penteno-*cyclo*heptanone (7.5 g., 0.05 *M*), Al(*iso*PrO)$_3$ (20.4 g., 0.1 *M* ; 500% excess) and anhydrous *iso*-PrOH (75 c.c.) was placed in a flask and a packed column (single-turn helices ; 100 mm. × 12 mm.) carrying a total-condensation-type still head was attached. This was heated under total reflux for ½ hour (min. temp. recorded, 75°) and then the distillation rate was adjusted (at *ca.* 1 drop/2 mins.). The acetone test became negative after a total of 60 hours, when the reaction mixture was cooled and treated with H_2SO_4 (C.P. H_2SO_4, 15 c.c. + water, 100 c.c. + ice, 250 g.). The separated oil was taken up in ether (50 c.c.) and petroleum ether (50 c.c.) ; this was washed with water (50 c.c.), $NaHCO_3$ in brine (5%, 50 c.c.) and dried. The solvent was removed and the residue fractionated to furnish a yellow liquid, b.p. 103°-109°/33 mm. (5.5 g.) ; a deep orange fraction of b.p. 134°/20 mm. (0.75 g.) was also collected, but not investigated. The chief product on rectification over sodium gave the diene as a colorless liquid, b.p. 100°/32 mm. ; n_D^{19}, 1.5250 ; yield 5.0 g. (Found : C, 89.35 ; H, 10.41. $C_{10}H_{14}$ requires C, 89.55 ; H, 10.44 per cent).

In the above experiment, when double the amount of Al(*iso*PrO)$_3$ was used, the acetone test became negative after 30 hours, and on working up, a mixture of the diene and the alcohol was obtained.

(*b*). *By the Dehydration of* Δ^9*-Octahydro-4-oxyazulene* : (*i*) *Dehydration with Sulphosalicylic Acid.*—The crude $LiAlH_4$-reduction product from the Δ^9-octahydro-4-oxoazulene (7.5 g., 0.05 *M*) was taken up in *n*-heptane (30 c.c.), sulphosalicylic acid dihydrate (100 mg.) added, and the mixture at once refluxed with continuous removal of water. Separation of water was practically over after 7 to 10 minutes, when the solution was immediately chilled in ice (a longer time of heating leads to polymerisation of the diene) and passed down a column of activated silica gel (−80, +100 mesh; 190 × 25 mm) ; this was washed with petroleum ether (60 c.c.). From these combined eluterates, the diene was isolated (fractionation under vacuum) as a colorless, mobile liquid, b.p. 90°−93°/20 mm. ; n_D^{28}, 1.5240 ; yield 5.4 g. Anderson and Nelson (*loc.cit.*) cite b.p. 72°/10 mm., n_D^{31}, 1.5250. It is very unstable and polymerisation soon

sets in. It gave a dirty-violet colour with bromine in acetic acid. On catalytic hydrogenation it showed the presence of 1.98 double bonds. An analytical sample had n_D^{26}, 1.5260. Light absorption in 95% ethanol : λ_{max_1}, 250 mμ, log ε, 3.85 ; λ_{max_2}, 255 mμ, log ε, 3.90 ; λ_{max_3}, 260 mμ, log ε, 3.89.

A mixture of diene (1.34 g.), maleic anhydride (freshly distilled, 2.94 g.) and anhydrous benzene (15 c.c.) was refluxed (20 hours.). The solvent was then distilled off and the residue treated with excess Na_2CO_3 solution (water-bath) ; the neutral portion (practically negligible) was removed by ether extraction and the acid liberated from the alkaline solution by acidification ; m.p. 119-20°, yield 1.96 g. Two recrystallisations (at 0°) from a mixture of benzene and petroleum ether gave colorless, prismatic rods of the dicarboxylic acid, m.p. 124-26° (the melt on solidification remelted at the same temperature), yield 1.0 g. (Found : C, 67.5; H, 7.2. $C_{14}H_{18}O_4$ requires C, 67.2 ; H, 7.2 per cent).

(*ii*) *Iodine-catalysed Dehydration*.—The crude alcohol (≡0.05 *M* of ketone) was distilled with iodine (20 mg.) at atmospheric pressure ; a mixture of hydrocarbon and water distilled over. When no more water had distilled, the residue and the distillate were combined, taken up in petroleum ether and after drying and partial removal of the solvent, filtered through a column of alumina (Basic/I ; 17 cm. × 1.7 cm.) which was washed with petroleum ether (50 c.c.). Removal of the solvent from the eluterate, followed by two rectifications over sodium, gave the diene, b.p. 92°-96°/30 mm. ; n_D^{26}, 1.5190. Light absorption in 95% ethanol : λ_{max_1}, 250 mμ, log ε, 3.79 ; λ_{max_2}, 255 mμ, log ε, 3.84 ; λ_{max_3}, 260 mμ, log ε, 3.80.

1 : 4 : 5 : 6 : 7 : 8-*Hexahydroazulene* (VI).—The Δ⁹-octahydro-1-oxoazulene (7.5 g., 0.05 *M*) was reduced with $LiAlH_4$ (095 g., 0.025 *M*) as detailed above for (II).

In a modified Claisen flask (3 c.c., column 3″) freshly fused and powdered $KHSO_4$ (100 mg.) was placed. This was heated in an oil-bath (140°) under vacuum (6 mm.). The above crude alcohol was let in dropwise during 2 minutes. By the time the addition was over, all the dehydrated material had distilled over (yellow distillate, yield 5.5 g.). The product on refractionation over sodium yielded the pure diene, b.p. 93°/30 mm.; n_D^{29}, 1.5110 ; yield 5.0 g. (74%). (Found : C, 89.45 ; H, 10.43. $C_{10}H_{14}$ requires C, 89.55; H, 10.44 per cent). Braude and Forbes (*loc. cit.*) record b.p. 56°/0.5 mm., n_D^{21}, 1.5129.

The diene (0.5 g.) was condensed with maleic anhydride as given for the isomeric hydrocarbon (III) ; the crude dicarboxylic acid (m.p. 124-30° ; 0.7 g.) on three crystallisations from a mixture of benzene (2 parts) and petroleum ether (one part) gave white crystals, m.p. 147-48°. (Found : C, 67.2 ; H, 7.2. $C_{14}H_{18}O_4$ requires C, 67.2; H, 7.2 per cent).

With bromine in acetic acid it give a dirty violet colour.

Decahydro-4-oxoazulene (cf. Hückel and Schnitzspahn, *Annalen*, 1933, **505**, 274).—The unsaturated ketone (I, 29 g.) in alcohol (70 c.c.) was shaken in an atmosphere of hydrogen at room temperature and pressure in the presence of palladium hydroxide-calcium carbonate catalyst (7.5 g., Busch, *Ber.*, 1916, **49**, 1603 ; 1929, **62**, 1458). The

reduction came to a close (1 hr.) after the absorption of 101% of the theoretical amount of hydrogen, when it was worked up to afford the desired compound as a colorless liquid, b.p. 96°/7 mm., yield 27 g. (93%). An analytical sample had n_D^{25}, 1.4880; d_4^{25}, 0.9942; M_D, 44.09 (calc. 44.01). (Found: C, 79.09; H, 10.65. $C_{10}H_{16}O$ requires C, 78.94; H, 10.52 per cent).

Decahydro-4-oxyazulene was prepared by the $LiAlH_4$ reduction of the above ketone by a method similar to the one described for (II), b.p. 104°/5 mm., 110°/7 mm.; n_D^{27}, 1.4970, yield 91-95%. For the alcohol, prepared by the Na and alcohol reduction, Plattner and Pfau (*Helv. Chim. Acta*, 1937, **20**, 224) record b.p. 126-28°/10 mm.; n_D^{20}, 1.504.

Octahydroazulene.—Dehydration of the above alcohol (6.0 g.) was carried out over $KHSO_4$ (1 g.) by the technique described above for the diene (VI); the temperature was 160°-165° and the pressure, 30 mm. The alcohol was dropped slowly at such a rate that the temperature of the distilling liquid was not higher than *ca.* 80°; this required 2½ to 3 hours. The distillate (5.2 g.) on fractionation yielded the hydrocarbon, b.p. 96-98°/37 mm.; n_D^{27}, 1.4900, yield 4.5 g. (84%) and some alcohol (0.5 g.) was recovered. With bromine in acetic acid the olefin gave a dirty brown colour. (Found: C, 88.11; H, 11.74. Calc. for $C_{10}H_{16}$: C, 88.2; H, 11.9 per cent). For the *trans*-Δ^4-octahydroazulene, Hückel and Schnitzspahn (*loc. cit.*) record b.p. 63.5°/8 mm., $n_{He}^{21.2}$, 1.4871.

Dehydrogenation.—The apparatus used for this purpose was similar to the one described earlier (Sukh Dev, *loc. cit.*, 1953, 729). The catalyst chamber was 18 cm. × 1 cm.; a tube (20 cm. × 0.8 cm.) was fused at the lower end to act as a condenser and the top carried a B14 socket. The dropping tube was of the same type, but had a capacity of 4 c.c. and was graduated in 0.5 c.c. portions; its dropping tip was sealed inside the B14 cone; the plug of its stop-cock had two deep scratches (*ca.* 8 mm.) starting from the bore and running in the opposite direction and it carried a long handle (*ca.* 4″); with this arrangement the rate of the flow of the diene could be conveniently adjusted. The joint should be lubricated only with a silicone-grease (meant for high temp. work) to avoid sticking of the joint. The temperature was measured by a thermometer placed alongside the catalyst bed in the furnace; the temperature of the furnace was regulated by a simmerstat control.

The catalyst chamber was packed with a mixture of 20% Pd—C (1 g.; Proc. D. of Organic Syntheses, Vol. 26, p. 78) and freshly ignited asbestos (*ca.* 0.5 to 0.75 cm. long; 2 g.); the packing was held in-between two asbestos plugs (1 cm.); the packing should neither be very dense nor loose.

The apparatus was assembled. The top of the dropping tube carried a three-way tube connected to a 'pop-valve' (mercury) and a supply of dry N_2. The air was displaced by nitrogen under suction (35-40 mm.) and the catalyst roasted at the temperature of dehydrogenation for one hour. The diene (2.68 g., 0.02 *M*; distilled over sodium just prior to use) was placed in the reservoir and dehydrogenation conducted. The condensate was taken up in petroleum ether (10 c.c.) and passed down a column of alumina (Basic/I; 120 × 18 mm.); this was washed with petroleum ether (60 c.c.) and

then with a mixture of petroleum ether and dry ether 4 : 1). The eluterates were collected into the colorless and blue portions. The solvent was removed and the blue crystalline residue (m.p. 90-92°) weighed ; from the colorless portion, undehydrogenated material could be recovered. For the runs giving much azulene (No. 4, 5, 6, 7), it was necessary to wash out the solid azulene with petroleum ether from the 'condenser' part of the catalyst tube ; this was then concentrated suitably and chromatographed over a bigger column (20 cm. × 2.5 cm.); a rechromatography was necessary in some cases. The azulene was then purified by sublimation at 30°-40°/1 mm. (m.p. 98-99°).

In the case of experiments using *p*-cymene (5 c.c. for 0.02 *M* of the compound) as a diluent, the azulene was isolated by Sherndal's method and then purified by chromatography ; when in this experiment (*vide supra*) the time of passage was reduced to 2 hours, the yield of azulene fell down from 7.6 to 4.6%.

Azulene should be stored either in the purest form or as a complex (with T. N. B., T. N. A. etc.) to avoid loss due to deterioration.

Picramide (T. N. A.) complex was prepared by adding azulene (0.2 g.), dissolved in acetic acid (1.5 c.c.) to a solution of TNA (0.35 g.) in acetic acid (3.5 c.c.) ; the mixture was warmed till clear and allowed to crystallise. The product (0.35 g., m.p. 175-77°) was collected and recrystallised from acetic acid to afford thick, black, prismatic rods, m.p. 176-78° with subliming out of azulene. (Found : C, 53.54 ; H, 3.41; N, 15.71. $C_{16}H_{12}O_6N_4$ requires C, 53.65 ; H, 3.37 ; N, 15.73 per cent).

The *complex with trinitrofluorenone* (T. N. F.) was prepared from azulene (100 mg.) and T. N. F. (200 mg.), dissolved in acetic acid (4 c.c.) containing water (0.2 c.c.) ; from this it separated as black leaflets, m.p. 161-63° with azulene subliming out ; yield 200 mg. (Found : N, 9.87. $C_{23}H_{13}O_7N_3$ requires N, 9.48 per cent).

The *non-azulenic portion* from the experiment No. 4 was purified by repeated distillation over sodium, when it had b.p. 90°-95°/30 mm. ; n^{26}, 1.5100 ; light absorption in 95% ethanol : λ_{max_1}, 250 mμ, log ε, 3.59 ; λ_{max_2}, 255 mμ, log ε, 3.62; λ_{max_3}, 260 mμ, log ε, 3.56. Its (1.34 g.) condensation with maleic anhydride (2.94 g.) by the procedure described for (III) gave a lot of polymerised neutral material and a dicarboxylic acid (500 mg.), m.p. 120-26° ; three crystallisations from a mixture of benzene and petroleum ether gave white flat needles (200 mg.), m.p. 148-49° ; mixed m.p. with the derivative from the diene (III) was 133-39°, while with that with the derivative from the hydrocarbon (VI) was undepressed.

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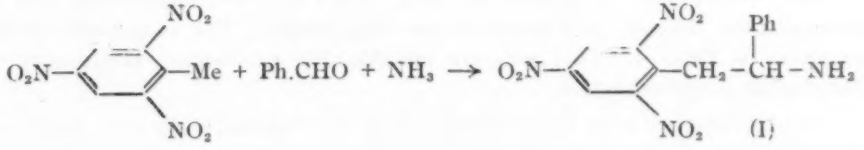
MANNICH AND KNOEVENAGEL REACTIONS INVOLVING THE ACTIVATING INFLUENCE OF NITRO GROUP

By V. Baliah and K. Ganapathy

2 : 4 : 6-Trinitrotoluene, *p*-nitrophenylacetic acid, its methyl and ethyl esters condense with aromatic aldehydes and ammonia to yield Mannich bases. These bases easily lose ammonia and often lead to the simultaneous formation of stilbene derivatives. 2 : 4-Dinitrophenylacetic acid reacts with benzaldehyde and ammonia, with decarboxylation, furnishing α-phenyl-β-2 :4-dinitrophenylethylamine; on longer heating, however, 2 :4-dinitrostilbene only can be obtained.

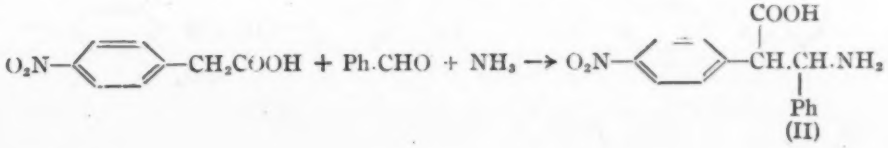
The α-methylene group in nitroalkanes is sufficiently reactive to undergo the Knoevenagel reaction (Knoevenagel, *Ber.*, 1904, **37**, 4502; Worral, *J. Amer. Chem. Soc.*, 1940, **62**, 3254; Fraser and Kon, *J. Chem. Soc.*, 1934, 604). The condensation of *p*-nitrotoluene with benzaldehyde (Chardonnens and Heinrich, *Helv. Chim. Acta*, 1939, **22**, 1471) illustrates the fact that vinylene linkages are capable of relaying the activating influence The methyl groups in 2 :4-dinitrotoluene and 2 :4 :6-trinitrotoluene are even more reactive, and these compounds readily undergo the Knoevenagel reaction (Thiele and Escales, *Ber.*, 1901, **34**, 2842; Pfeiffer and Monath, *ibid.*, 1906, **39**, 1306). Several aromatic nitro compounds containing reactive methyl or methylene groups have been used in the Mannich reaction (Mannich and Stein, *Ber.*, 1925, **58**, 2659; Kermack and Muir, *J. Chem. Soc.*, 1933, 300; Bruson and Butler, *J. Amer. Chem. Soc.*, 1946, **68**, 2348) to obtain N-substituted β-arylethylamines. In the present work 2 :4 :6-trinitrotoluene, *p*-nitro- and 2 :4-dinitro-phenylacetic acid, and their methyl and ethyl esters have been condensed with several aromatic aldehydes and ammonia. Glacial acetic acid or absolute ethanol was used as a solvent.

The condensation of benzaldehyde with 2 :4 :6-trinitrotoluene and ammonia yielded the amine (I). Piperonal reacted similarly.

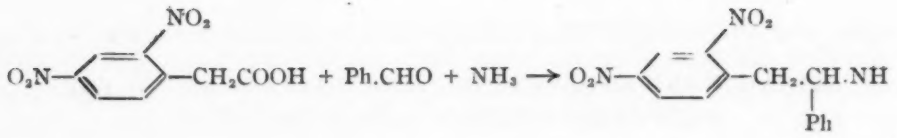


(I)

The products obtained with *p*-nitro- and 2 :4-dinitro-phenylacetic acids depended upon the time of heating. When the reactants were heated for a short period (5 minutes), there was no decarboxylation with *p*-nitrophenylacetic acid, whereas 2 :4-dinitrophenylacetic acid lost CO_2. The reaction proceeds according to the following equations :

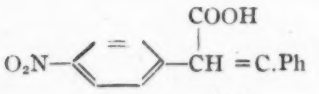


(II)

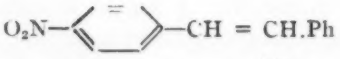


(III)

If the heating of the reactants is continued for a longer period (30 minutes), the products are not Mannich bases but stilbene derivatives. In the case of *p*-nitrophenyl acetic acid, there is a partial decarboxylation, and a mixture of α-4-nitrophenylcinnamic acid (IV) and 4-nitrostilbene (V) is obtained.



(IV)



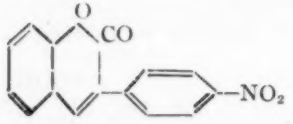
(V)

The two can be separated by means of sodium carbonate solution. In the case of 2 : 4-dinitrophenylacetic acid, 2 : 4-dinitrostilbene alone was obtained. The formation of the unsaturated compounds indicates that the Mannich bases lose ammonia on longer heating and suggests that the Mannich reaction is an intermediate step in the Knoevenagel reaction.

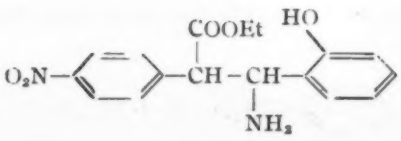
The base (III) was found to be unstable. Its acetyl and benzoyl derivatives, obtained directly from its hydrochloride, are, however, stable. They did not undergo the Bischler-Napieralsky reaction when refluxed with phosphorus oxychloride. Instead, 2 : 4-dinitrostilbene was obtained. This seems to be a general behaviour of αβ-diarylethylamines. Similar observations were made by Dey and Ramanathan (*Proc. Nat. Inst. Sci. India*, 1943, **9**, 193). Furthermore, electron-attracting groups such as $-NO_2$ are known to inhibit the cyclisation (Morgan and Walls, *J. Chem. Soc.*, 1938, 389 ; 1945, 18 ; B.P. 511,353/1940).

The condensations of methyl and ethyl esters of *p*-nitrophenylacetic acid with several aromatic aldehydes and ammonia were also studied. The compounds prepared are listed in Table I. The bases are unstable oily substances. Hence, they were characterised as hydrochlorides.

Salicylaldehyde, being an *o*-hydroxyaldehyde, behaved differently from other aldehydes. When condensed with *p*-nitrophenylacetic acid or its methyl or ethyl ester and ammonia, the product was 3-*p*-nitrophenylcoumarin (VI). With the ethyl ester, the base (VII) also could be isolated as its hydrochloride.



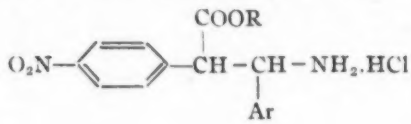
(VI)



(VII)

TABLE I

β-Alkoxycarbonyl-β-p-nitrophenyl-α-arylethylamine hydrochlorides.



No.	R.	Ar.	Solvent.	Refluxed for.	Yield.	M.P.	Formula.	% Carbon Found.	% Carbon Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	% Chlorine. Found.	% Chlorine. Calc.
1.	Et	Ph	AcOH	5 min	30%	204-205°	$C_{17}H_{19}O_4N_2Cl$	57.9	58.2	5.3	5.4	10.2	10.1
2.	Et	4-$CH_3OC_6H_4$	EtOH	30	17	188°	$C_{18}H_{21}O_5N_2Cl$	56.8	56.8	5.7	5.5	9.3	9.3
3	Et	3 : 4-$(CH_2O_2)C_6H_3$	EtOH	10	25	182-85°	$C_{18}H_{19}O_6N_2Cl$	54.9	54.8	4.9	4.8	9.3	9.0
4.	Et	3 $O_2NC_6H_4$	EtOH	10	26	187-88°	$C_{17}H_{18}O_6N_3Cl$	51.3	51 6	4.7	4 6	9 3	9.0
5.	Et	4-$CH_3C_6H_4$	EtOH	30	15	206-208°	$C_{18}H_{21}O_4N_2Cl$	59.0	59.3	5.7	5.8	10 0	9 7
6.	Et	2-HOC_6H_4	EtOH	2	4	251-53°	$C_{17}H_{19}O_5N_2Cl$	55.3	55.7	5.5	5.2	10.0	9 7
7.	Me	Ph	AcOH	5	15	212-13°	$C_{16}H_{17}O_4N_2Cl$	56.8	57.1	5.1	5.1	10.5	10.6
8.	Me	3 : 4-$(CH_2O_2)C_6H_3$	AcOH	2	27	202-204°	$C_{17}H_{17}O_6N_2Cl$	53.7	53.6	4.7	4.5	9.7	9.3
9.	Me	4-$CH_3OC_6H_4$	AcOH	2	8	208-210°	$C_{17}H_{19}O_5N_2Cl$	55.4	55.7	5.0	5.2	9.4	9.7
10.	Me	4-$CH_3C_6H_4$	MeOH	10	14	220-21°	$C_{17}H_{19}O_4N_2Cl$	58.1	58.2	5.3	5.4	10.4	10.1

EXPERIMENTAL

α-Phenyl-β-2 : 4 : 6-trinitrophenylethylamine Hydrochloride.—A mixture of 2 : 4 : 6-trinitrotoluene (5.7 g.), benzaldehyde (2.7 g.), dry ammonium acetate (2 g.) and glacial acetic acid (10 c.c.) was refluxed for 5 minutes and left overnight. The dark brown product was dissolved in ether and treated with HCl (conc., 3 c.c.) and a few drops of water. The precipitated hydrochloride was filtered off and washed with ether. It crystallised from ethanol as colorless needles (2 g., 23%), m.p. 204-205°. (Found: C, 45.6; H, 3.5; Cl, 9.9. $C_{14}H_{11}O_6N_4Cl$ requires C, 45.5; H, 3.5; Cl, 9.6 per cent). The *base* was unstable.

The *acetyl derivative* of the base was obtained by refluxing the above hydrochloride, acetic anhydride and fused sodium acetate for about 10 minutes. Purification from ethanol gave light yellow crystals, m.p. 184°. (Found: C, 51.1; H, 3.9. $C_{16}H_{14}O_7N_4$ requires C, 51.3; H, 3.7 per cent).

The *benzoyl derivative* crystallised from ethanol as colorless needles, m.p. 164-65°. (Found: C, 57.5; H, 3.7. $C_{21}H_{16}O_7N_4$ requires C, 57.8; H, 3.7 per cent).

α-3 : 4-Methylenedioxyphenyl-β-2 : 4 : 6-trinitrophenylethylamine Hydrochloride.—Ammonium acetate (3.85 g.), 2 : 4 : 6-trinitrotoluene (11.4 g.), piperonal (7.5 g.) and glacial acetic acid were heated to boiling and left for a day. The product was then dissolved in ether and the hydrochloride was precipitated by the addition of hydrochloric acid. The yield was 6.2 g. (30%). Recrystallisation from ethanol gave colorless needles, m.p. 193-95°. (Found: C, 43.7; H, 3.3; Cl, 8.9. $C_{15}H_{13}O_8N_4Cl$ requires C, 43.6; H, 3.2; Cl, 8.6 per cent).

β-Amino-α-p-nitrophenyl-β-phenylpropionic Acid (II).—A mixture of *p*-nitrophenylacetic acid (18 g.), benzaldehyde (10.6 g.), ammonium acetate (7.7 g.) and glacial acetic acid (25 c.c.) was heated to boiling and allowed to stand for a day. The resulting reddish brown liquid was treated with ether and the ether-insoluble product was filtered off, washed well with ether and dried. The yield was 6 g. (19%). It crystallised from water as fine needles, m.p. 175-76°. (Found: C, 55.8; H, 5.3. $C_{15}H_{14}O_4N_2.2H_2O$ requires C, 55.9; H, 5.6 per cent). The water of crystallisation could not be removed even after drying the substance under reduced pressure in a drying istol at 110° for 2 hours.

Its *methyl ester hydrochloride* was prepared as follows. The acid was suspended in absolute methanol, saturated with dry HCl gas, and left overnight. The excess of methanol was evaporated off and the residue was washed with water. Recrystallisation from ethanol-ether gave colorless needles, m.p. 211-12°. There was no depression in melting point on admixture with the hydrochloride of the base, prepared by condensing methyl *p*-nitrophenylacetate, benzaldehyde and ammonia. (Found: C, 57.0; H, 5.1. $C_{16}H_{17}O_4N_2Cl$ requires C, 57.1; H, 5.1 per cent).

4-Nitrostilbene and α-4-Nitrophenylcinnamic Acid.—A mixture of *p*-nitrophenylacetic acid (4.5 g.), benzaldehyde (2.7 g.), ammonium acetate (2 g.) and glacial acetic

acid (10 c.c.) was refluxed for 1 hour and left overnight. The product was extracted with ether and the ether evaporated off. The residue was shaken with sodium carbonate solution and filtered. Crystallisation of the residue (0.35 g.) from ethanol gave 4-nitrostilbene, m.p. 154-55°. Pfeiffer and Sergievskaja (*Ber.*, 1911, **44**, 1109) report m.p. 155°. The sodium carbonate extract on acidification with HCl gave a light yellow solid (0.4 g.) which on recrystallisation from dilute acetic acid was found to be α-4-nitrophenylcinnamic acid, m.p. 223-24°. Walther and Wetzlich (*J. prakt. Chem.*, 1900, *ii*, **61**, 181) report m.p. 224.5°.

4-Nitro-4'-methoxystilbene and α-p-nitrophenyl-p-methoxycinnamic acid were obtained in 6% and 5% yields respectively by condensing *p*-nitrophenylacetic acid with anisaldehyde as in the previous case. The compounds melted at 131-32° and 231-32°. Pfeiffer (*Ber.*, 1915, **48**, 1794) and Hewitt, Lewcock and Pope (*J. Chem. Soc.*, 1912, **101**, 608; 1931, 444) report m.p.s 132-34° and 231°.

β-2 : 4-Dinitrophenyl-α-phenylethylamine.—2 : 4-Dinitrophenylacetic acid (16.8 g.) (Borsche, *Ber.*, 1909, **42**, 3596), benzaldehyde (11.3 g.), ammonium acetate (9 g.) and glacial acetic acid (20 c.c.) were refluxed for 5 minutes and left overnight. The product was dissolved in ether and saturated with HCl. The precipitated *hydrochloride* (15.5 g., 52%), on recrystallisation from ethanol, gave long colorless needles, m.p. 231-32°. (Found : C, 51.8; H, 4.1; Cl, 10.9. $C_{14}H_{14}O_4N_3Cl$ requires C, 51.9; H, 4.3; Cl, 11.0 per cent).

The base, when liberated from the hydrochloride by dissolving the latter in ethanol and adding ammonia, gradually became reddish brown and resinous. It could not be purified.

The *benzoyl derivative*, prepared by using the hydrochloride itself, crystallised in colorless needles from ethanol, m.p. 202-203°. (Found : C, 64.7; H, 4.4. $C_{21}H_{17}O_5N_3$ requires C, 64.5; H, 4.3 per cent).

The *acetyl derivative* was prepared by treating the hydrochloride with pyridine and acetic anhydride. Light yellow crystals, melting at 158-59°, were obtained from ethanol. (Found : C, 58.3; H, 4.7. $C_{16}H_{15}O_5N_3$ requires C, 58.4; H, 4.6 per cent).

Preparation of β-Alkoxycarbonyl-β-p-nitrophenyl-α-arylethylamine Hydrochlorides.—A mixture of *p*-nitrophenylacetic ester (0.05 *M*), the aldehyde (0.05 *M*) and ammonium acetate (0.05 *M*) in glacial acetic acid or absolute ethanol (20 c.c.) was heated under reflux for 2 to 30 minutes and left for a day. The solvent was then removed, if it was ethanol. The product was dissolved in ether and saturated with HCl. The hydrochloride crystallised out slowly. It was filtered off and washed with a little water. The recrystallisation was effected in ethanol or ethanol-ether (for details see Table I).

3-p-Nitrophenylcoumarin.—Ethyl *p*-nitrophenylacetate (2.1 g.), salicylaldehyde (1.2 g.), ammonium acetate (1 g.) and 95% ethanol (10 c.c.) were refluxed for 15 minutes and left overnight. The yellow solid (2.8 g., 98%) which separated crystallised as golden yellow needles from acetic acid, m.p. 262°. Borsche (*loc. cit.*) reports the same melting point.

When methyl *p*-nitrophenylacetate and *p*-nitrophenylacetic acid were used in place of ethyl *p*-nitrophenylacetate, the yields were 50% and 30% respectively.

Ethyl α-2 : 4-*Dinitrophenyl*-m-*nitrocinnamate*.—Condensation of ethyl 2 : 4-dinitrophenylacetate (2 g.), *m*-nitrobenzaldehyde (1.2 g.) and ammonium acetate (1 g.) in absolute ethanol (10 c.c.) furnished this compound (1.5 g., 50%). It crystallised as yellow needles from ethanol, m.p. 153-54°. (Found: C, 52.4; H, 3.4. $C_{17}H_{13}O_8N_3$ requires C, 52.7; H, 3.4 per cent).

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STUDIES IN INDIGOID DYES. PART XIV. THIOINDIGOID DYES DERIVED FROM DIPHENYL-4 :4′-DISULPHONIC ACID

By Paresh Chándra Dutta and Dasrath Mandal

4 : 5-Diphenyl-(3″-hydroxy-1″-thiophene)-4′-thioglycollic acid (I), prepared from diphenyl-4 : 4′-disulphonic acid, has been condensed with various *o*-diketones, and the corresponding thioindigoid dyes obtained with the object of studying colour and its relation to chemical constitution.

In Part XIII of this series (this *Journal*, 1954, **31**, 827), thioindigoid dyes derived from diphenyl-4-monosulphonic acid were described. It was expected that the *bis*-thioindoxyls due to the presence of two indigoid chromophores in the same molecule would produce indigoid dyes of much deeper in colour and brighter in shade. With this object in view the present investigation was undertaken to prepare the *bis*-thioindoxyl from diphenyl-4 : 4′-disulphonic acid and obtain from it *bis*-thioindigoid dyes corresponding to the mono-thioindigoids, prepared from diphenyl-4-monosulphonic acid, so that a comparison of colour may be made between these two series of dyes.

bis-Thioindoxyls, which are functionally capable of affording polymeric thioindigoid dyes, are not very common in the literature. Eighteen such dyes, all obtained from the three benzene-*o*-*bis*-thioindoxyls, have been described (U.S.P. 2, 094, 595/1940). Leandri (*Gazzetta*, 1949, **79**, 286) has described the formation of naphtho-1 : 8-5 : 4-*bis*-thioindoxyl, although in a very poor yield, from naphthyl-1 : 5-dithioglycollic acid, but its further reaction with *o*-diketones has not been studied. Naphtho-2 : 1-6 : 5-*bis*-thioindoxyl has also been described (Friedländer, **14**, p. 927). Corbellini and Albenga (*Gazzetta*, 1931, **61**, 111), while attempting to cyclise the *bis*-thioglycollic acid, obtained from naphthaline-1 : 5 dithiol, could effect it only partially, *i. e.*, one thioglycollic acid side-chain out of the two had only cyclised. The finding of the authors in the present investigation has been in agreement with that of Corbellini and Albenga and that with 4 : 4′-diphenyldithioglycollic acid, prepared from diphenyl-4 : 4′-disulphonic acid through disulphochloride, dimercaptan etc., the cyclisation takes place with one thioglycollic acid side-chain only, yielding a mono-thioindoxyl glycollic acid (I) instead of a *bis*-thioindoxyl. This is proved from the fact that this thioindoxyl reacts with only one molecular quantity of *o*-diketones forming mono-thioindigoids. The indifference of one thioglycollic acid side-chain to cyclisation, of the two present in the same molecule, may be attributed to the formation of a lactone (II) in this case also, as suggested by Corbellini and Albenga in the case of naphthyl-1 : 5-dithioglycollic acid (*loc. cit.*).

The diphenyl-4 : 4′-disulphonic acid (*Annalen*, 1862, **122**, 209; Feldman, *Helv. Chim. Acta*, 1931, **14**, 751) was prepared by the method described in the experimental, as the methods referred to above had given rise to an impure product containing monosulphonic acid and producing an impure sulphochloride of m.p. 203° (*Ber.*, 1880, **13**, 386;

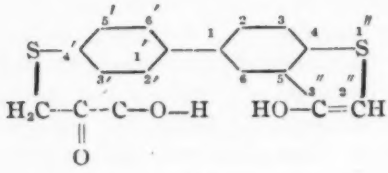
Feldman, *loc. cit.*), whereas the disulphochloride, prepared by us from pure disulphonic acid, melts at 211°. The preparation of disulphochloride from diphenyl directly by the chlorosulphonic acid method (*Monatsh.*, 1930, **55**, 358) was not found at all convenient. Again, the reduction of disulphochloride to dimercaptan with tin and hydrochloric acid (*Ber., loc. cit.*) gave an extremely poor yield, but Corbellini and Albengas' method (*loc. cit.*) furnished about 80% yield.

The thioindoxyl thioglycollic acid (I) produces a blue dye (III) on oxidation with potassium ferricyanide in alkaline solution, which is insoluble in organic solvents, probably due to its being the sodium salt. All these dyes dissolve in alkaline hydrosulphite usually with a yellow colour and the original dyes are reproduced on oxidation. These also dissolve in concentrated sulphuric acid with a characteristic colour. These dyes are insoluble in alcohol, slightly soluble in acetic acid and fairly soluble in nitrobenzene. Although these are not *bis*-thioindigoid dyes, these have been found to produce slightly deeper shade on cotton when compared with such dyes obtained from diphenyl monosulphonic acid, as the following table shows.

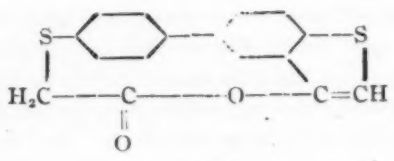
TABLE I

2 : 2′-*bis*-5-Phenylthiophene-indigo	...	Pinkish violet
Sodium-*bis*-4 : 5-diphenylthioindigo-4 : 4′-dithioglycollate	...	Blue
2-(5-Phenylthionaphthene)-3′-indol-indigo	...	Pinkish violet
Diphenyl-4 : 5-thiopheno-4′-thioglycollic acid-3′-indol-indigo	...	Violet
2-(5-Phenylthionaphthene)-2′-acenaphthylene-indigo	...	Light pink
Diphenyl-4 : 5-thiopheno-4′-thioglycollic acid-2′-acenaphthylene-indigo		Pinkish violet
2-(5-Phenylthionaphthene)-ethylene-indigo	...	Violet
bis-Diphenyl-4 : 5-thiopheno-4′-thioglycollic acid-ethylene-indigo	...	Bluish violet

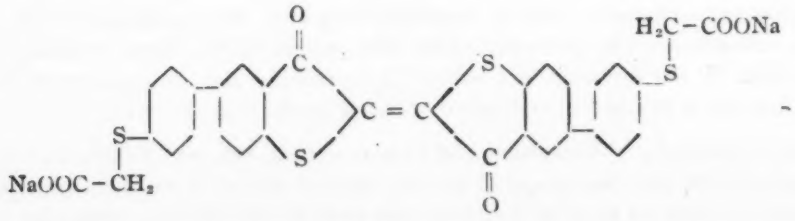
The structures of these dyes may be represented by the following formulae :



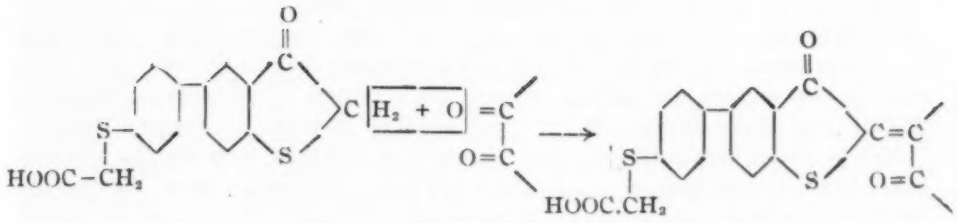
(I)



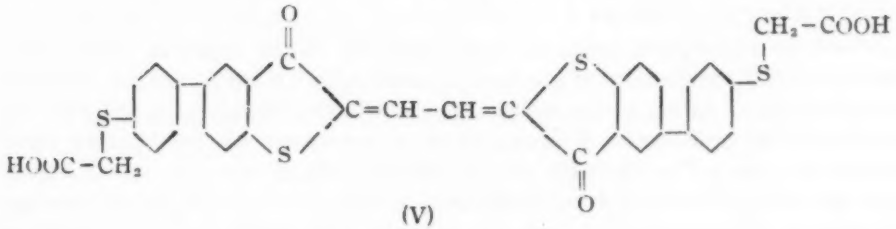
(II)



(III)



o-Diketone. (IV)



(V)

EXPERIMENTAL

Diphenyl-4 : 4′-disulphonic acid was prepared by the method of Feldman (*loc. cit.*) modified in the following way. Finely divided diphenyl (15.4 g.) was mixed with H_2SO_4 (conc., 25 g.) and the mixture heated in an oil-bath at 140° for 2 hours. To the thick dark liquid, after cooling, enough water was added to dissolve the sulphonic acids. The unchanged diphenyl separating as an oil in the surface was allowed to cool when it solidified and was removed by filtration. The acid filtrate was then boiled with excess of fine copper oxide and filtered hot. Most of the copper salt of the disulphonic acid (soluble in hot water) was obtained in the filtrate. The almost insoluble copper salt of the monosulphonic acid, left behind as a residue, was twice extracted with boiling water to obtain the residual copper salt of the disulphonic acid. The combined filtrate was then concentrated to a small bulk and treated with potassium carbonate till alkaline, and boiled ; the precipitated copper carbonate and oxide were removed by filtration and the filtrate, after further concentration, treated with potassium chloride for complete separation of the di-acid potassium salt. This potassium salt was then thrice crystallised from hot water, and thus obtained in a very pure condition, yield 80-85%.

Diphenyl-4 : 4′-disulphochloride.—The method (*Ber.*, 1880, **13**, 386) has been modified and the following method adopted. Carefully dried and finely powdered potassium diphenyl-4 : 4′-disulphonate (40 g.) was mixed with PCl_5 (55 g.) and $POCl_3$ (10 c.c.) with copious evolution of HCl fumes. The mixture was heated in an oil-bath at 140° for 1 hour, $POCl_3$ distilled off under reduced pressure and the mixture decomposed by ice and left overnight. The solid residue was finely powdered, filtered, and thoroughly washed with water. It was crystallised from toluene as long colorless needles, m.p. 211°. Yield of the pure product was 32 g. (Found : C, 41.2 ; H, 2.5. Calc. for $C_{12}H_8O_4S_2Cl_2$: C, 41.02 ; H, 2.27 per cent).

Diphenyl-4 : 4′-dithiol was prepared by a method analogous to that of Corbellini and Albenga (*loc. cit.*). Absolute alcohol (50 c.c.) after previous drying over quick lime was saturated with dry HCl gas, and to this stannous chloride crystals (25 g.) were added and the solution kept boiling. Now to this a solution of diphenyl-4:4′-disulphochloride (5 g.) in dry benzene (50 c.c.) was added in portions. A vigorous reaction took place during each addition. After the addition had been complete, the mixture was refluxed for one hour more and about half the volume of the liquid distilled off. During the whole process the flow of HCl gas was continued. On cooling, the dithiol crystallised out from the residual liquid. It was filtered, washed thrice with strong HCl and then with water, yield 3 g.

Diphenyl-4 : 4′-dithioglycollic acid was prepared in the following way. 4 : 4′-Dithiol (4.36 g.) was dissolved in caustic soda solution (50 c.c., 10%) and to the filtrate monochloroacetic acid (4 g.), previously neutralised with caustic soda solution, was added, and the mixture after dilution with 50 c.c. more water was warmed on a water-bath for an hour. The sparingly soluble di-sodium salt of the acid soon began to separate. The whole mixture was then diluted with a large volume of water, boiled and filtered hot. The residue was repeatedly extracted with boiling water and the filtrate acidified with HCl each time whereby the thioglycollic acid was obtained as a voluminous white precipitate. It was filtered, washed and dried, yield 5.8 g.

4 : 5-*Diphenyl* -(3″-*hydroxy*-1″-*thiophene*)-4′-*thioglycollic Acid* (I).—4 : 4′-Dithioglycollic acid (4 g.) was suspended in dry petroleum ether (40 c.c., b.p. 60°-80°) and to this PCl_5 (5.6 g.) and pyridine (2 drops) were added. The mixture was refluxed on a water-bath for an hour when a vigorous evolution of HCl gas was noticed. The solution after filtering from a little undissolved sticky solid was cooled in a refregerator when gradually the acid chloride, first separated as an oil, later solidified to white flakes, m.p. 65°-66°. This solid was filtered, dissolved in fresh petroleum ether (40 c.c.) and treated with $AlCl_3$ (anhydrous, 4 g.) in small portions. The mixture was then refluxed on a water-bath till the evolution of HCl gas had ceased. After cooling, the petroleum ether was carefully poured out and the chocolate-red complex decomposed by crushed ice and HCl (conc.). A brownish yellow substance was thus obtained but this could not be obtained in a pure condition due to its susceptibility to oxidation. From dilute acetic acid the thioindoxyl separated out as a yellowish white mass with no sharp melting point, m.p. ranging between 189° and 203°, so that for condensation with *o*-diketones this impure sample had to be used. Its formula has been based on the analytical results of its condensation products with *o*-diketones.

Sodium bis-4 : 5-*Diphenylthioindigo*-4 : 4′-*dithioglycollate* (III).—The above thioindoxyl (2 g.) was dissolved in 5% NaOH solution and filtered. The filtrate was treated with potassium ferricyanide solution until the separation of the substance as a blue precipitate was complete. It was filtered and washed with water but could not be purified as it had been found completely insoluble in organic solvents and water. The compound dissolved in alkaline hydrosulphite with a greenish yellow colour and dyed cotton in blue shade. Just like the sodium salt of the dithioglycollic acid, this sodium salt appeared to be insoluble.

Diphenyl-4 : 5-thiopheno-4′-thioglycollc acid-3-indol-indigo (IVa).—To an acetic acid solution of (I) was added isatin, dissolved in acetic acid, when the yellowish brown solution immediately changed to blood-red and on heating violet-red precipitate began to separate out. HCl (0.5 c.c.) was then added and the mixture boiled for 15 minutes more to ensure complete reaction. The precipitate was then filtered, and washed with acetic acid and alcohol. It was then crystallised from nitrobenzene as a violet crystalline mass, m.p. above 310°. It dissolves in H_2SO_4 (conc.) with a greenish brown colour and dyes cotton from light yellow alkaline hydrosulphite vat in violet shade. (Found : C, 64.6 ; H, 3.6. $C_{24}H_{15}O_4NS_2$ requires C, 64.72 ; H, 3.37 per cent).

Diphenyl-4 : 5-thiopheno-4′-thioglycollic acid -3-(5 : 7-dinitro)-indol-indigo (IV b), 3-(6-bromo)-indol-indigo (IV c), -2′-acenaphthylene-indigo (IV d), -2′-(5′ or 6′-nitro)-acenaphthylene-indigo (IV e), -2′-(5′ or 6′-bromo)-acenaphthylene-indigo (IV f), -2′-(5′ or 6′-dinitro)-acenaphthylene-indigo (IV g), -9-phenanthrene-indigo (IV h), -1′-aceanthrylene-indigo (IV i) and ethylene-indigo (V) * were prepared in the same way as described above (IV a) from (I) with the respective *o*-diketones as recorded in Table II. The compounds were all crystallised from nitrobenzene and were dissolved in H_2SO_4 (conc.) with characteristic colour and dyed cotton with various shades of colour as shown in Table II. In the preparation of the last compound 5 c. c. of HCl (conc.) was used.

TABLE II

Structure. No.	O-Diketones	M.P.	Colour with conc. H_2SO_4	Dying shade	Mol. formula.	% Carbon Found.	% Carbon Calc.
IV b	5 :7-Dinitroisatin	215°	Green	Dark chocolate shade	$C_{24}H_{13}O_8N_3S_2$	N :7.53	7.85
IV c	*m*-Bromoisatin	>290°	Greenish brown	Pinkish violet	$C_{24}H_{14}O_4NS_2Br$	C :54.73 H : 2.81	54 96 2.67
IV d	Acenaph-thenequinone	>300°	Green	Do	$C_{26}H_{16}O_4S_2$	C :70.38 H : 3 4	70.0 3 33
IV e	5-Nitroacenaph-thenequinone	>310°	Do	Light blue	$C_{29}H_{15}O_6NS_2$	C :63 81 H : 3.08	64.0 2.86
IV f	5-Bromo do	160°	Do	Pink	$C_{28}H_{15}O_4S_2Br$	C :59 92 H : 2.81	60 1 2.68
IV g	5 :6-Dinitro-do	>300°	Brown	Greenish grey	$C_{28}H_{14}O_8N_2S_2$	C :58.72 H : 2.65	58.95 2.46
IV h	Phenanthrene-quinone	>300°	Violet-brown	Chocolate brown	$C_{30}H_{16}O_4S_2$	C :71.0 H : 3.68	71 14 3.55
IV i	Aceanthra-quinone	>300°	Greenish brown	Copper-red	$C_{32}H_{18}O_4S_2$	C :72.31 H : 3.59	72.45 3.40
V	* Glyoxal sodium bisulphite	>300°	Brownish violet	Bluish violet	$C_{34}H_{22}O_6S_4$	C :62.16 H : 3.51	62.38 3 36

* (In acetic acid soln. with 5 c.c. of conc. HCl).

The authors express their sincere thanks to Dr. B. D. Tilak, Professor oi Dyestuff Technology, Bombay University, and Principal M. Q. Doja of the Science College, Patna, for their keen interest in this investigation and to Dr. T. S. Gore, Dept. of Chemical Technology, Bombay University, for the micro-analysis of some of the compounds described in this paper.

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CHEMICAL INVESTIGATION OF INDIAN *COTONEASTER FRIGIDA*, WALL. PART I. CHEMICAL COMPOSITION OF FRUIT PULPS

By Sachindra Kumar Datta

Chemical composition of the fruit pulps of *Cotoneaster frigida*, Wall of Darjeeling has been determined by analysing its various components, such as moisture, ash, fat, pentosan, hydrocyanic acid, benzaldehyde, protein, pectic acid and reducing sugar. The fruits are a very rich source of *d*-sorbitol.

The plant *Cotoneaster frigida*, Wall belongs to the N. O. Rosaceae. It is a tree nearly twenty feet high and grows in various temperate regions of the world. In India, it is found in central and eastern Himalayas and in the interior of Sikkim at an altitude between 7000 and 9000 ft. The plant is widely distributed at Darjeeling and its surrounding places and Senchal lake area of Ghoom, and is locally known as 'Latgeri.' The tree is erect, decidious having straight, almost horizontal branches. The leaves are 3″ to 5″ in length, oblong and narrowed to the base. The tree bears numerous flowers in cymes and the fruits are small globose scarlet berries with double seeded stones. The wood of this plant is of much commercial importance, being heavy, smooth, elastic and even grained. The twigs are suitable for turning and may be used for making walking sticks, golfclubs, axe handles, bows and agricultural implements, like other varieties of Cotoneaster (Hooker, "Flora of British India," II, p. 384).

Many plants belonging to the N.O. Rosaceae, specially the Cotoneasters, are characterised by the general presence of hydrocyanic acid in them. Rosenthaler (*Pharm. Acta Helv.*, 1926, **1**, 167; 1929, **4**, 196) detected the presence of hydrocyanic acid in the vegetative parts of a large number of plants, including *Cotoneaster melanocarpa*, *C. nummuloria*, *C. buxifolia*, *C. horizontalis*, *C. francheti*, etc. Plouvier (*Compt. rend.*, 1937, **205**, 1433; *Ann. Sci. nat. Bot.*, 1942, **3**, 204) reported the presence of HCN and enzymes in 84 types of Rosaceae plants, including *C. frigida*, Wall. The fruits of many species of Cotoneaster indicated the presence of amygdonitrile glucoside from the determination of glucose : HCN ratio (*Compt. rend.*, 1936, **202**, 352). Ripe berries of *Cotoneaster* (*pyrocantha*) *angustifolia* exhibited the presence of γ-carotene and prolycopenes, which were extracted with the help of methyl alcohol (Zechmeister *et al.*, *J. Biol. Chem.*, 1942, **144**, 315; *J. Amer. Chem. Soc.*, 1947, **69**, 1930). Ascorbic acid content of the fruits of some Cotoneaster were determined by Johansson (*Expt. Sta. Record*, 1940, **83**, 718). *d*-Sorbitol was extracted by Strain (*J. Amer. Chem. Soc.*, 1937, **59**, 2264) from the fruits of some Cotoneaster plants, including *C. frigida*. The chemical composition of the wood of *C. vulgaris* was determined by Shokov and Sobetski (*J. Appl. Chem. USSR.*, 1948, **21**, 659) with a view to ascertaining the nature of its cellulose. So, apart from the determination of HCN in the form of amygdonitrile and extraction of sorbitol, no record of any systematic work on *Cotoneaster frigida*, Wall, is found in the literature. Kirtikar and Basu describe a plant, *C. nummularia*, of the same species, as expectorant and stomachic ("Indian Medicinal Plants", vol. II,

p. 991). Though *C. frigida* does not enjoy any repute in medicine, a thorough chemical examination of the various parts of this plant of India has been undertaken by the present author with a view to exploring its utility by finding out any other active principle, in addition to sorbitol and cyanogenatic glucoside. The chemical composition of the fruit pulps forms the subject matter of the present communication.

The plants at Darjeeling bear fruits, generally, at the end of August and the fruits become matured and juicy in October and November, when the branches are covered with clusters of numerous small scarlet berries, which begin to drop down with the beginning of winter. The plant and its fruits were identified by Sri S. N. Mitra, Curator of Lloyd Botanical Garden, Darjeeling.

Experimental

The seeds, constituting 25% of the weight of the fresh fruits, were separated from the fruits and the pulp on drying in air lost 72% moisture. The loss of moisture from air-dried pulps on drying in an electric oven at 110° was 5.52%, this indicating a total loss of 73.54% in the fresh pulp. The air-dried pulp was powdered to pass through a 60-mesh sieve and stored in a glass jar as a stock sample. The stock sample (75 g.) on subjecting to soxhlet extraction (3 hours each time) with different solvents furnished several fractions as recorded in Table I.

Table I

	Solvents used.		Solvent-free extrct (% on moisture-free sample).	
1.	Petroleum ether (40°-60°)	...	...	2.15
2.	Ether	...	...	1.29
3.	Chloroform	...	...	0.76
4.	Ethyl acetate	...	...	0 24
5.	Alcohol (90%)	...		
			(Solid wax-like mass) 46.7	60 1
			(Red-brown semi-solid) 13.4	
6.	Benzene	...	...	0.44
7.	Acetone	...	...	1 4

Petroleum ether extract.—The yellow extract on evaporation and drying in vacuum afforded a yellow powder having aromatic odour. It became sticky on exposure to moist air. The extract contained fats and amygdonitrile glucoside.

Ether extract.—The residue was a powdery, yellowish white solid having bitter taste and showed positive carbohydrate reaction. It may also contain amygdonitrile glucoside.

Chloroform extract.—The residue was a brown gummy mass. It may contain resinous and colouring matters.

Alcohol extract.—The extract on keeping for two days deposited white, soft, crystalline, wax-like, water-soluble substance. The mother-liquor on evaporation left a red-brown liquid mass, which on keeping in vacuum changed to a semi-solid matter. Both the substances were found to contain *d*-sorbitol.

Benzene extract.—The residue was dark brown thick oily mass. It may contain resinous matter.

Acetone extract.—It was a yellowish white waxy-solid and was found to contain a trace of sorbitol.

The detailed study of the various extractives will form the subject of a subsequent communication.

Ash-content and Mineral Matters.—Ash content was determined by incineration of the original air-dry sample in a big platinum crucible. The colour of the ash obtained was grey with greenish patches. Preliminary qualitative analysis of the ash indicated the presence of Ca, Fe, K, Cu, P, SiO_2 etc. The alkalinity of the ash was determined by treatment with 0.1*N*-HCl (excess) in a crucible and warming on a steam-bath, cooling and titrating the excess acid with 0.1*N*-NaOH. The alkalinity of the ash has been reported as number of ml. of *N*-acid required to neutralise 1 g. of ash (Table II).

Acidity of the Fresh Sample: (*a*) *Titratable Acidity.*—The fresh fruit pulp (100 g.) was boiled with 500 c.c. water for 1 hour, replacing at intervals the water lost by evaporation. The mixture was cooled, filtered and the filtrate made up to one litre, 25 c.c. of which was diluted to 100 c.c. and titrated just below the end-point with 0.1*N* alkali, using 0.3 c.c. of 1% phenolphthalein solution as an indicator. The nearly neutral solution (2.5 c.c.) was diluted to 25 c.c. in a separate beaker (by this extra dilution, the colour of the fruit extract became so pale that phenolphthalein colour was distinctly visible) and the titration was completed by adding more alkali. The titration value has been reported as c.c. of 0.1*N* alkali/100 g. of fresh sample (Table II).

(*b*) *Volatile Acidity.*—The original sample (fresh pulp, 25 g.) was distilled in a current of steam for 2 hours into a measured excess of 0.1*N*-NaOH ; the excess of alkali was then titrated with 0.1*N*-HCl. The result has been expressed as before (Table II).

Fat content.—The stock sample was soxhletted with a mixture of alcohol-benzene (1 : 1) for about 6 hours. The solvent-free extract contained in addition to fatty matters, a negligible amount of colouring substances and a small quantity of sorbitol. These were however, removed by repeated washing of the residue with hot pyridine. The sorbitol-free residue on drying furnished the actual fat content, calculated on moisture-free basis (Table II).

Protein and Hydrocyanic Acid.—Nitrogen content generally indicates the presence of protein matter, but as these fruits contain cyanogenatic glucoside, the total nitrogen obtained by the usual Kjeldahl method will not entirely represent its protein content. So, the amount of HCN in the sample (both in fresh and air-dried pulps) was determined first and then the nitrogen present in the dried residue was estimated by Kjeldahl method. It was found that about 0.91% of nitrogen was present in the sample, both fresh and dry, calculated on moisture-free basis, and hence, the protein content of the pulps was 5.7%. Hydrocyanic acid in the sample (both fresh and air-dried) was determined by the following method (*J. Amer. Chem. Soc.*, 1915, **37**, 601) :

A large quantity of the sample (50 g. air-dried and 100 g. in case of fresh pulp) was macerated with about 200 c.c. of water at room temperature for two hours in a

distilling flask and the mixture was steam-distilled with 100 c.c. more water; the distillate was collected in 50 c.c. of 0.02*N*-$AgNO_3$, acidified with 1 c.c. of dilute HNO_3. When 200 c.c. of the distillate had been collected, it was filtered through a Gooch crucible, washed with water, and the excess of $AgNO_3$ in the filtrate was titrated with 0.02*N*-KCNS, using ferric alum indicator (1 c.c. of 0.02*N*-$AgNO_3 \equiv 0.054$ g. of HCN).

Benzaldehyde.—Amygdonitrile was found present which could be extracted from the pulps by ether extraction. A considerable amount of the original sample (50 g. air-dried and 100 g. in case of fresh pulp) was hydrolysed as before with water and the benzaldehyde formed was distilled with steam. When 200 c.c. of the distillate had been collected, 20 c.c. of the phenylhydrazine solution (3 c.c. acetic acid, 40 c.c. water and 2 c.c. freshly distilled phenyhydrazine) was added to it. The mixture was allowed to stand overnight in dark and then filtered through a weighed Gooch crucible, washed with cold water and finally with 10% alcohol. The precipitate was dried in a vacuum desiccator over sulphuric acid for 24 hours in the dark and weighed as 0.5408 g. of benzaldehyde. The mean of four such estimations was taken (*J. Assoc. Off. Agrl. Chem.*, 1936, **19**, 182; 1941, **24**, 63). The weight of benzaldehyde was found slightly less than four times the amount of HCN obtained. It appears that in addition to amygdonitrile, some other cyanogenatic glucosides may also be present in traces, in the pulps.

Sorbitol.—The solid wax-like mass, obtained from the alcohol extract (Table I) of the air-dried sample, was dissolved by heating four times its weight of pyridine. The solution was kept in a vacuum desiccator for two days, when shining white fibrous crystals of sorbitol-pyridine compound (Strain, *loc. cit.*) appeared, which were separated by filtration. The crystals were washed with cold pyridine and dried over H_2SO_4 in a vacuum desiccator. A similar crop of the sorbitol-pyridine compound was obtained from the mother-liquor. The crystals melted at 90°. The red-brown mass which was also obtained from the alcohol extract was dissolved in alcohol and boiled under reflux with animal charcoal. The alcohol-free filtrate was then extracted with hot pyridine. The solution on keeping in a refrigerator deposited the crystals of sorbitol-pyridine compound, m.p. 89°. In this way sorbitol was isolated from the alcohol-extract of the fruit-pulps, as far as possible. The total quantity of the pyridine-free dry sorbitol (m.p. 91-92°) was weighed.

Pectic Acid.—Pectic acid was determined in the fresh sample of fruit-pulps (*J. Assoc. Off Agrl. Chem.*, 1934, **17**, 66) as follows:

An aliquot (250 c.c.) of the same solution as was used for acidity determination was taken in a beaker; sucrose (15 g.) was added to it and the volume was reduced to 30 c.c. by evaporation. To this hot solution EtOH (200 c.c.) was immediately added with constant stirring. The voluminous precipitate which appeared was allowed to settle and then filtered and washed with alcohol. The precipitate was transferred with hot water into the original beaker, and the volume was again reduced to about 40 c.c. After cooling the solution to 10°, 50 c.c. of 1% NaOH solution was stirred into it. The mixture was allowed to stand for 15 minutes after which were added

to it 40 c.c. water and 10 c.c. of HCl (1 + 2.5) and then it was boiled for 5 minutes. The precipitated pectic acid was filtered and washed with hot water and then transferred to a platinum crucible, dried on a steam-bath and finally in an oven at 100° to a constant weight. It was ignited, the loss in weight indicated the weight of pectic acid.

Total Reducing Matters.—Reducing matter in the fruit pulps, both in the fresh and air-dried samples, was determined by the method of Munson-Walker (*J. Amer. Chem. Soc.*, 1906, **28**, 663; 1907, **29**, 541). For the estimation of soluble reducing sugars in the fresh pulps, 100 c.c. aliquot of the prepared solution was taken in a beaker and to it was added an excess of saturated neutral lead acetate solution; the mixture was allowed to stand and filtered. To the filtrate was added dry sodium oxalate to precipitate the excess lead used in clarification. The precipitate was again filtered and sugar was estimated in the filtrate by the above mentioned method, using Fehling solutions. To determine the total quantity of soluble sugar, a further amount of the clarified deleaded solution was hydrolysed at room temperature with 20 c.c. of HCl (1:1) for 24 hours (Methods of Analysis, A.O.A.C, 1950, p. 338) and then it was exactly neutralised with NaOH (conc.) and sugar was estimated in it as before. Sugar was also determined in air-dried pulps. An extract of the air-dried material was prepared as described under 'Titratable acidity'. Reducing sugar was determined as before in aliquot quantities of this solution, first in the unhydrolysed solution and then in solutions hydrolysed by HCl. All the results have been expressed in terms of the amount of *d*-glucose per 100 g. moisture-free pulps.

Estimation of Pentosan.—Furfural was estimated in the original air-dried sample as phloroglucide by the method of Schorger (Dorée, "Methods of Cellulose Chemistry", 1933, p. 361). The pentosan content was derived from the furfural yield by using Krober's formula (Norris and Resch, *Biochem. J.*, 1935, **29**, 1594):

$$\text{Pentosan} = \frac{\text{furfural} \times 100}{64.3}.$$

Estimation of Cellulose.—The original sample (air-dry) was extracted successively with petroleum ether, chloroform, alcohol-benzene (1:1) and alcohol (90%). The extracted material was used for cellulose determination. The cellulose content was first determined by the method of Cross and Bevan (*J. Chem. Soc.*, 1889, **55**, 199). The sodium chlorite method was also used for its estimation. Extracted sample was treated with 1% sodium chlorite solution for about 4 hours at 96-97° (solid-liquor ratio = 1:50) at p_H between 4 and 5, using acetic acid and sodium acetate buffer (Sarker, *Proc. Nat. Inst. Sci. India*, 1946, **12**, 23; Das, Mitra and Wareham, *ibid.*, 1951, **17**, 37). The fibre was filtered in a sintered glass crucible, washed and dried at 105°-110° to a constant weight. Then it was ignited, the loss in weight was taken to be the actual weight of cellulose. It was found that Cross and Bevan's method gave a lower yield (16.8%) of ash-free cellulose, while the sodium chlorite method gave a higher yield (18.2%), calculated on moisture- free basis.

The summary of the chemical analysis of the pulps is recorded in Table II, where only the average values of the experiments, done in triplicate, are recorded.

4—189oP—6

TABLE II

Chemical composition of the fruit pulps.

Constituents.	Particulars of the sample used.	Percentage (corrected to non-defatted pulp on dry basis).	Percentage (on fresh pulps).
1. Moisture (110°)	Original, air-dried	5.2	73.54
2. (a) Ash	Do	3.63	0.96
(b) Alkalinity of the ash	Do	21.6 ml. *N*-acid/1 g. ash	...
3. Hydrcyanic acid	Do	0.321	0.085
Do	Fresh pulp	0.362	0.097
4. Benzaldehyde	Original, air-dried	1.202	0.318
Do	Fresh pulp	1.4	0 370
5. (a) Nitrogen	Original, air-dried	0 90	0 238
Do	Fresh pulp	0.93	0.246
(b) Protein	Original, air-dried	5.62	1.49
Do	Fresh pulp	5.81	1.54
6. Sorbitol	Dry basis	43.48	11.5
7. Fat	Original, air-dried	0.54	0.143
8. Acidity of the sample:			
(a) Volatile	Fresh pulp	...	32.03 c c. 0.1 *N*-alkali/100 g.
(b) Titratable	Do	...	80.55 c c. 0.1 *N*-alkali/100 g.
9. Pectic acid	Do	5.3	1.4
10. (a) Reducing sugars (soluble)	Do	6.2	1.64
(b) Do	Original, air-dried	7.1	1.87
(c) Do (after hydrolysis)	Fresh pulp	8.9	2.3
(d) Do (after hydrolysis)	Original, air-dried	10.3	2.7
11 Pentosan	Do	13.6	3.6
12. Cellulose (ash-free)	De-fatted		
(a) Cross and Bevan		16.8	4.4
(b) Sodium chlorite method		18.2	4.8

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STUDIES IN THE REACTION BETWEEN LEAD NITRATE AND POTASSIUM NITRITE

By D. G. Vartak and M. B. Kabadi

The conductometric and thermometric titrations have been performed between the solutions of potassium nitrite and lead nitrate of different molar concentrations. The results indicate that the two salts combine to form in solution molecular compounds of the composition: (*i*) $4KNO_2.Pb(NO_3)_2$, (*ii*) $2KNO_2.Pb(NO_3)_2$ and (*iii*) $KNO_2.Pb(NO_3)_2$

The behaviour of lead nitrate in solutions of alkali nitrites does not appear to have attracted sufficient attention. Meldrum (*J. Chem. Soc.*, 1908, **83**, 24, 97), who investigated the reaction between KNO_2 and lead salts, prepared the compounds of Hayes (*Quart. J. Chem. Soc.*, 1861, **13**, 335) and assigned to it the approximate composition $K_2Pb(NO_2)_3.NO_3.H_2O$.

Experimental

Merck's A. R. quality potassium nitrite (93% pure, containing NO_3' and Cl' as impurities) was purified by the method of Oza and Walawalkar (this *Journal*, 1943, **20**, 315). The crystals of KNO_2, which were collected in different operations of the method, were dried in a desiccator over calcium chloride. The sample, on analysis of NO_2', was found to be 99.90% pure when tested for nitrite.

Measurement of Electrical Conductivity.—Conductivity of different solutions containing lead nitrate (Merck's A. R. quality, recrystallised) and potassium nitrite in various molar proportions was measured by Kohlrausch's method. The method was modified so that 3 to 230 volt transformer could be used to step up the current that was fed into the galvanometer with a shunt, through a simple triode valve serving as a rectifier. The resistance of the shunt was increased so that accurate readings could be recorded by means of a Moll type galvanometer using the lamp and scale arrangement. The reflected beam of light moved on the scale in a certain direction on sliding the contact on the bridge wire, but when the null point was passed, it moved immediately in the opposite direction. The conductivity bridge was provided with a point contact, the wire of which was calibrated, as also the resistance box. The conductivity cell, which was a U-tube about 10 c.c. capacity, had the cell constant 0.2943. The cell constant was checked before and after every set of readings. The measurements were carried out at $30° \pm 0.1°$ of solutions containing 10 c.c. of KNO_2 to which different volumes of lead nitrate solution were added, and the total volume made to 30 c.c. The results are recorded in Table I in which 'λ' stands for molar conductivity of KNO_2 and x, the number of c.c. of lead nitrate added.

TABLE I

'x'.	1.0 M-KNO_3; 1.0 M-Pb $(NO_3)_2$.		1.0 M-KNO_3; 0.5 M-Pb $(NO_3)_2$.		0.5 M-KNO_3; 1.0 M-Pb$(NO_3)_2$.	
	$K \times 10^3$.	λ.	$K \times 10^3$.	λ.	$K \times 10^3$.	λ.
0.0 c.c.	3.859	115.77	3.859	115.77	2.014	120.84
0.5	3.984	119.52	3 922	117.66	2.149	128.94
1.0	4.162	124.86	3.987	119 61	2 279	136.74
1.25	...	...	...	...	2.442	146.52
1.5	4.311	129.33	4 071	122.13	2.475	148.50
2.0	4.554	136.62	4 165	124.95	2 550	153.00
2.5	4 837	145.11	4.237	127.11	2.643	158 59
3.0	4.917	147.51	4.317	129.51	2.702	162 12
3.5	5.008	150.24	4.427	132.81	2.803	168.18
4 0	5.130	153 90	4.561	136.83	2.875	172 50
4.5	5.273	158.19	4.698	140 88	2.976	178.56
5.0	5.462	163.86	4.844	145 32	3.141	188 46
6.0	5.598	167.94	4.921	147.63	3.220	193 20
7.0	5.729	171 87	5.013	150.39	3 300	198.00
8.0	5.855	175.65	5.138	154.14	3.381	202.86
9.0	6.091	182 73	5.275	158 25	3.462	207 72
10.0	6.363	190 89	5.470	164.10	3.545	212.70
11 0	6.480	194.40	5.553	166 59	3.626	217.56
12 c	6.601	198 03	5 607	168.21	3.709	222 54
13.0	6.719	201.57	5.669	170.07	3.795	227.70
14.0	6.839	205 17	5.732	171 96	3.878	232.68
15.0	6.953	208.59	5.796	173.88	3.959	237.54
16.0	7.071	212.13	5 861	175.83	4 045	242.70
17.0	7 187	215.61	5.920	177.60	4.127	247 62
18.0	7.294	218.82	6.091	182.73	4.210	252.60
19.0	7.387	221.61	6.229	186.87	4 295	257.70
20.0	7 504	225.12	6.368	191.04	4.375	262 50

Thermometric Titrations.—The different solutions were kept in a thermostat to attain the room temperature. The temperature of the two solutions were noted before mixing. The titrations were carried out in a thermos flask in which known volumes of the two reagents were mixed ; the total volume was kept constant by adding the required volume of water to the reagents taken in the thermos. The contents were quickly stirred and the maximum departure from the initial temperature was noted. The initial temperature was the mean of the temperatures of the two mixing reagents. For noting the temperature differences, a Beckmann thermometer was used. The solutions of the two reagents used were the same as employed for the conductivity measurements. The results are shown in Table II, in which x denotes c.c. of KNO_3 solution ; m and m_1 denotes mols. of KNO_3 and lead nitrate in solution respetively and d, the difference in temperature.

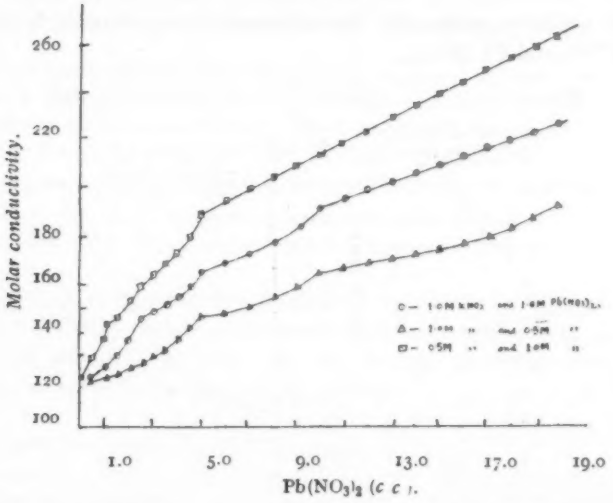
TABLE II

Pb $(NO_3)_2$ added.	x = 30 c.c. m = 0.03			x = 30 c c. m = 0 03			x = 30 c c. m = 0.015		
	m_1.	d.	m_1/m.	m_1.	d	m_1/m.	m_1.	d.	m_1/m
1 0 c c.	0 0010	+0.07	0.0333	0.0005	+0.06	0.01667	0.0010	+0 07	0.0667
2.5	0.0025	+0 08	0.0833	0.00125	+0 065	0 0416	0.0025	+0.08	0.1667
5.0	0.0050	+0.09	0.1667	0.0025	+0 070	0.0833	0 0050	+0.10	0.3333
7.5	0 0075	+0 10	0 2500	0 00375	+0.080	0 125	0 0075	+0.12	0 5000
10 0	0.0100	+0.13	0 3333	0.0050	+0.080	0.1667	0.0100	+0 18	0 6667
12.5	0.0125	+0.16	0 4167	0.00625	+0 090	0.2083	0 0125	+0.25	0 8333
15.0	0.015	+0 20	0.5000	0.0075	+0 095	0.2500	0.015	+0 32	1.0000
20.0	0.020	+0.33	0 6667	0 0100	+0.12	0 3333	0.020	+0 31	1.3300
25.0	0 025	+0.47	0.8333	0.0125	+0 15	0.4167	0.025	+0.30	1.6657
30.0	0.030	+0.61	1.0000	0.0150	+0 18	0.5000	0.030	+0.29	2.0
35.0	0 035	+0 59	1.1667	0.0175	+0.24	0.5833	0.035	+0.28	2.333
40.0	0.040	+0.57	1.3333	0 0200	+0.31	0.6667	0.040	+0.27	2.6667
45.0	0.045	+0.55	1.5000	0 0225	+0.37	0 7500	0.045	+0 26	3 0
50 0	0.050	+0.53	1.6667	0.0250	+0 43	0.8333	0.050	+0.25	3.333
60.0	0.060	+0.49	2.0000	0.0300	+0.56	1.0000	0.060	+0.24	4.0

DISCUSSION

The study of the data recorded in Table I shows that with the addition of increasing amounts of lead nitrate, molecular conductivity of the solutions goes on steadily rising. But this rise is found to take place in three stages which is very clearly shown in curves (Fig. 1) in which the molar conductivity of solutions is plotted against the volume of lead nitrate solution added. These breaks appear to mark the formation of a

FIG. 1



molecular compound between potassium nitrite and lead nitrate. The molecular ratios of KNO_2 and $Pb(NO_3)_2$ corresponding to the three breaks respectively are 4 : 1, 2 : 1 and 1 : 1. From the three breaks observed, the molar ratios of the two combining salts are calculated to furnish the composition of the compound formed. The results are recorded below.

TABLE III

Volume of KNO_2 solution taken = 10 c.c.

Molar conc. of soln. of		$Pb(NO_3)_2$ soln. (c.c.) corrsp. to the break			Molar ratio KNO_2 : $Pb(NO_3)_2$ at the break		
KNO_2.	$Pb(NO_3)_2$.	*i*	*ii.*	*iii.*	*i.*	*ii.*	*iii.*
1.0	1.0	2.5	5 0	10.0	4 :1	2 :1	1 :1
1 0	0 1	5.0	10.0	20.0	4 :1	2 :1	1 :1
0.5	1.0	1.25	2 5	5.0	4 :1	2 :1	1 :1

These results show that the three different molecular compounds are formed depending upon the amount of lead nitrate present in the mixture, and their probable compositions respectively are : (*i*) 4 KNO_2. $Pb(NO_3)_2$; (*ii*) 2 KNO_2. $Pb(NO_3)_2$ and (*iii*) KNO_2. $Pb(NO_3)_2$.

From Table II it appears that the difference in temperature increases at first with the addition of lead nitrate till a maximum point is reached. After this point, a slow

decrease in difference of temperature, which reaches the minimum, is observed. After the minimum point is reached, further addition of lead nitrate does not cause any noticeable alteration in "difference of temperature". It is remarkable that the rise in "difference of temperature" also takes place in three stages in the thermometric study. In the first stage, the "increase in difference of temperature" is rather slow. In the next, it is rapid, whereas in the third stage, it is still more rapid. The behaviour observed here is in complete conformity with that observed in conductivity measurements. The study on the thermometric titrations therefore agrees with the findings made earlier regarding the formation and composition of molocular compounds between KNO_2 and $Pb(NO_3)_2$.

FIG. 2

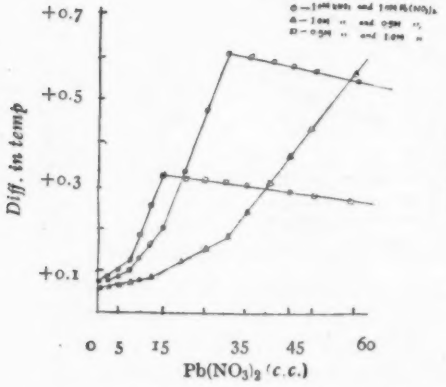
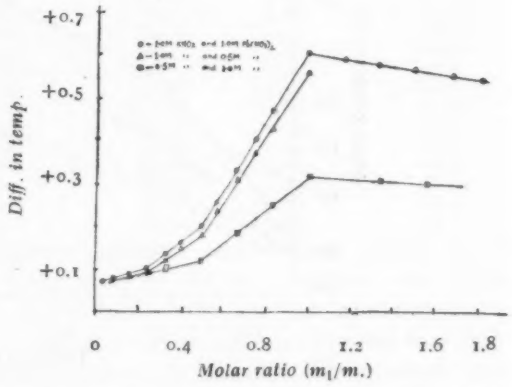


FIG. 3



The behaviour of the solutions in thermometric titrations is clearly brought out in curves in Fig. 2 in which the difference in temperature is plotted against the c.c. of lead nitrate added. These curves are made up of intersecting straight lines, the points of intersection denoting the composition of the molecular compounds formed. Further confirmation about the formation and composition of the compound is obtained by plotting (*i*) molar conductivity against the molar ratio of the reagents and (*ii*) difference in temperature against the molar ratio (Fig. 3). These curves are self-explanatory.

It is thus concluded from the study of electrical conductivity and the thermometric titrations that the molecular compounds formed in the solutions containing KNO_2 and $Pb(NO_3)_2$ have the composition: (*i*) $4KNO_2.Pb(NO_3)_2$, (*ii*) $2KNO_2.Pb(NO_3)_2$ and (*iii*) $KNO_2.Pb(NO_3)_2$ respectively.

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THE STUDY OF IMPERFECT COMPLEXES. PART III. THE CUPRAMMINE COMPLEX. A CALORIMETRIC STUDY BY JOB'S METHOD OF CONTINUOUS VARIATION AND BY SIDDHANTA'S MODIFIED METHOD OF CONTINUOUS VARIATION

By Sushil Kumar Siddhanta and Mrityunjay Prasad Guha

The complex formation between copper sulphate and ammonia has been studied calroimetrically by Job's method of continued variation, as also by Siddhanta's modification of Job's method, using the molar heat content as the indicative property. The composition of the complex has been found to be $Cu(NH_3)_4^{2+}$ and its dissociation constant at about 30° is approximately 3×10^{-9} (mean value).

The experimental technique used for the calorimetric measurements has been described in details.

The defects inherent in the simple thermometric titration method of Dutoit for the purpose of determining the composition of compounds formed in solution, have been pointed out and discussed.

Dutoit's method of thermometric titration (*J. chim. phys.*, 1921, **19**, 324) has found a rather wide application to detect the formation of new compounds, particularly those which are only stable in solution. In this method, the solution of a compound B is added by instalments of δx c.c. to a certain volume 'a' c.c. of a solution of another compound A, taken in a Dewar flask, and the corresponding temperature changes, read on a Beckmann thermometer, are plotted against the volume 'x' c.c. ($x = \Sigma\delta x$) of B added; the inflexion points on the corresponding T/x curve are taken to correspond to the composition of the compounds formed between A and B.

The present authors, however, are of opinion that such a simple method is not often a reliable guide as to the composition of compound or compounds formed, for the following reasons:

(*a*) It has been noted in course of the present work that abrupt temperature changes of the burette solution do take place within the period of titration in spite of all precautions.

(*b*) In cases of formation of imperfect complexes of the type $A_m B_n$, the reaction of B with A is not quantitative, and hence, the heats evolved, when plotted against the respective volumes of B added, will not yield a straight line curve and the amounts of heat $\delta(-\Delta H)$ evolved for successive equal additions of δx c.c. of B will gradually diminish; the heat evolution continues even after the theoretical inflexion point as considerable amount of unreacted A is present even then. The $-\Delta H/x$ curve (and consequently the T/x curve) therefore takes a gradual bend which continues considerably beyond the theoretical inflexion point, there being no sharp inflexion. Thus, the non-linear middle portion of the curve, extending over a fairly large region, may often give the impression of more than one inflexion point where there should be really one. Such misjudgments are liable to occur, particularly in cases where two or more complexes, each of low stability, are formed.

(*c*) In cases of even perfect complexes of the type AB_n having a large value of n, though we add a concentrated solution of B, the value of the liquid in the Dewar near the inflexion point is much greater than that present initially, causing a much smaller temperature rise towards the end for the liberation of the same amount of heat. Even when n in AB_n is small, the temperature rise due to successive small but equal additions, δx c.c., of B is not proportional to the corresponding heat change, $\delta(-\Delta H)$, as the volume of the solution in the Dewar increases continuously.

If, however, heat of reaction $(-\Delta H)$ is utilised as the guide for determining the maximum concentration of the complex, employing Job's method of continued variation (*Compt. rend.*, 1925, **180**, 928; *Ann. chim.*, 1928, *x*, **9**, 113), a reliable information about the composition and dissociation constant of an imperfect complex can be derived, as has already been discussed by one of us (Siddhanta, Part I, this *Journal*, 1948, **25**, 580). The advantage of this new method over Job's original spectrophotometric method has also been discussed. A similar suggestion, though in a very rudimentary form, had already been expressed by Chauvenet, Job and Urbain (*Compt. rend.*, 1920, **171**, 855). Reference to the above work has been missed in Part I of this series partly because of faulty abstraction of the above work in the *British Chemical Abstracts* (1920, **180**, *ii*, 757) and partly because Job's original paper on his method of continued variation (*loc. cit.*) does not contain any reference to the earlier work, containing the very basis of Job's method of continued variation. It may, however, be mentioned that while Chauvenet *et al.* have made a mere suggestion that the heat of reaction can be used as an indicative property to be studied in the method of continued variation, Siddhanta (*loc. cit.*) has expressed the idea on a sound thermodynamical basis.

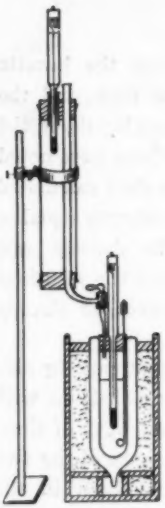
Job's method, as such, cannot be used in a continuous titration process, for which the modification suggested by Siddhanta (Part II, this *Journal*, 1948, **25**, 584) has been found to be well suited for determining the composition and the dissociation constant of imperfect complexes. The advantage of Siddhanta's modification over Job's lies chiefly in making the experimental work simpler and much more rapid without loss in accuracy. Particular mention may be made of the fact that the time for taking one complete set of readings in Job's method using extinction coefficient, conductivity or refractivity as the guiding property, *can be reduced from a period of about ten days to one of about half an hour*, by employing Siddhanta's modification using molar heat content as the indicative property.

Experimental

Apparatus.—One of the parent solutions was taken in a cylindrical Dewar flask (capacity 150 c.c.), which was placed in a wooden box, packed with asbestos powder, as shown in Fig. 1. The Dewar is fitted with a three-bored cork, through which pass the discharge nozzle of a burette, a Beckmann thermometer and a glass stirrer, bent into the shape of a small ring at the bottom and provided with a small cork at the top so as to minimise heat conduction when operated by hand. The other solution is added from the burette, which is enclosed by a very wide jacket-tube of glass fitted with a rubber stopper at both ends. The jacket-tube is completely filled with water, the temperature of which can

be noted by another Beckmann thermometer to be introduced into it from the top through a small glass tube, passing through the upper rubber stopper.

FIG. 1



Water Equivalent of the Dewar Flask.—The Dewar was used as the calorimeter and its water equivalent was found out electrically. Since the material of the calorimeter was glass, its water equivalent differed with the volume of the liquid present in it. Distilled water (100 c.c., 75 c.c. and 50 c.c. respectively) was successively taken in the Dewar and a current C at a voltage E was passed through a fine manganin wire (the total weight of the wire was only 0.5 g. and hence its heat capacity was negligible) completely immersed in water for t seconds in each case, and the water equivalent of the Dewar (W) was calculated by using the formula

$$G+W=\frac{E.C.t.}{4.185\times\Delta T}$$

where ΔT is the rise in temperature noted by a Backmann thermometer, and G is the number of grams of water present. The experiments were repeated by varying E and t, and the mean values of W (neglecting fractions) were 20, 15 and 10 calories/degree for the corresponding volume of the water taken in the Dewar, viz., 100, 75 and 50 c.c. respectively. Thus, the water equivalent can safely be assumed as one fifth of the volume of the liquid taken in the Dewar.

Procedure.—The experiments were all carried out in a room free from draught so as to avoid fluctuations in temperature during experiments. To start with, the Dewar was half filled with water and the two Beckmann thermometers (B_I and B_{II}) and a tenth degree thermometer were kept immersed in it for about 15 minutes, and the readings on each were carefully noted. Let A, B and θ be the readings on the above three thermometers respectively. Thus, if A' be any reading on Beckmann B_I, the actual temperature, correct to the tenth of a degree, should be $(A'-A+\theta)^\circ$; similarly any reading B' on the Beckmann B_{II} should represent $(B'-B+\theta)^\circ$, correct to the tenth of a degree.

The parent solutions of copper sulphate and ammonia of requisite strengths, noted at the tops of the respective tables, were prepared from reagent quality materials (E. Merck). Solutions, slightly more concentrated than necessary in the actual experiments, were initially prepared (copper sulphate and ammonia solutions having been determined iodimetrically and alkalimetrically respectively) and then these solutions were diluted with calculated amounts of water so as to yield solutions of the desired strengths.

In each of the parent solutions of copper sulphate and ammonia were dissolved required amounts of solid ammonium sulphate so that each solution became $M/2$ with respect to the latter; the addition of ammonium sulphate was necessary to prevent the precipitation of copper hydroxide or basic copper sulphate during mixing. Since both

the solutions were $M/2$ with respect to ammonium sulphate, no dilution of the latter was involved in the process of mixing the two solutions, and hence, no heat of dilution for ammonium sulphate was needed to be taken into account.

Job's Method of Continuous Variation

Copper sulphate solution of strength 'c' ($100-x$ c.c.) was added from the burette to 'x' c.c. of ammonia solution at a concentration, 'pc', taken in the Dewar flask, and the temperature T_1 of the copper sulphate solution was noted with the Beckmann B_I; the initial and final temperatures, T_2 and T_3 respectively, of the solution in the Dewar were noted by the Beckmann B_{II}. The temperature change, ΔT, *due to reaction*, was then calculated (vide Tables I, II and III), and the heat of reaction ($-\Delta H$) was evidently equal to 120. ΔT, the volume of the solution mixture being always 100 c.c. (The density and specific heat of the solution mixture were both taken to be unity since the solutions were very dilute; water equivalent of the Dewar was equal to 20 cal./degree, as already stated.).

Before beginning any experiment, the parent solutions were both kept side by side in a draught-free room for half an hour; the jacket of the burette was filled up with water and kept beside the parent solutions in the same room for the same length of time. This step was taken to minimise, as far as possible, the temperature difference of the two parent solutions before mixing. The two parent solutions were then taken in the burette and the Dewar respectively, and about 15 minutes were allowed for the burette solution to attain the temperature of the water jacket. Then after noting the temperatures T_1 and T_2, the requisite volume of the burette solution was quickly added into the Dewar, and the mixture vigorously stirred for exactly two minutes. The final temperature, T_3, which attained a constant value by this time, was then noted. In noting the temperatures, a reading lens was used and the third decimal place was read by eye estimation. A trained eye can read a temperature correct to $\pm$ 0.002° on a Beckmann thermometer.

The results for equimolecular parent solutions (both $M/10$) have been summarised in Table I, and those for non-equimolecular parent solutions in Tables II and III. The values ΔT were plotted against $X(=100-x)$. The resulting curves are shown in Fig. 2; curves I, II and III correspond to Tables I, II and III respectively. The values of ΔT were plotted against X in the curves, since ΔT was directly proportional to ($-\Delta H$), the volume of the mixture being always 100 c.c.

The composition of the complex was found out to be Cu: $NH_3 = 1:4$, from the maximum point of the curve I (obtained with equimolecular parent solutions) at $x = 80$ c.c., so that

$$m/n = \frac{100-x}{x} = \frac{20}{80} = \frac{1}{4},$$

m and n refer to the reaction $mA + nB \rightleftharpoons A_mB_n$, where A and B are the reacting molecules (vide Part I, *loc. cit.*).

Thus knowing the values of m and n, the dissociation constant K of the complex was calculated from the maximum points in the curves II and III, obtained from non-equimolecular parent solutions using the formula (vide Part I, *loc. cit.*)

$$K = \frac{c^{m+n-1} \cdot p^{n-1} \cdot \{(pm+n)x - n\}^{m+n}}{m^{m-1} \cdot n^{m-1} \cdot (p-1)^{m+n-1} \cdot \{n-(m+n)x\}}.$$

The results obtained from curves II and III are shown below :

Curve.	c.	p.	x for maximum point of the curve.	K (approx.).
II	0.1	2	68	4×10^{-9} at 28°
III	0.05	4	53	3×10^{-9} at 30.5°

Fig. 2

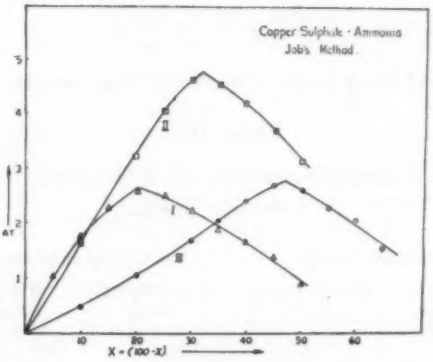


TABLE I

Titration of M/10 ammonia soln. with M/10 copper sulphate soln. (Job's method).
($c = 0.1$. $p = 1$).

$M/10$-$CuSO_4$		$M/10$-NH_4OH		Final temp. of the mixture T_3 (Beckmann B_{II}).	Calc. mean initial temp. of the mixture, T_4 * (assuming no reaction).	Rise in temp. $\Delta T = T_3 - T_4$.
Vol. added $(100-x) = X$ c.c	Temp. T_1 (Beckmann B_I).	Vol. taken in Dewar (x c.c.).	Initial T_2 (Beckmann B_{II}).			
5	27.522	95	27.672	27.760	27.666	0.094
10	27.850	90	27.570	27.759	27.593	0.166
15	28.003	85	27.597	27.880	27.648	0 232
20	28.245	80	27.669	28.019	27.765	0.254
25	28.335	75	27.760	28.128	27.879	0.249
30	28.415	70	27.821	28.191	27.970	0.221
35	28.477	65	27.902	28.260	28.070	0.190
40	28.470	60	27.843	28.215	28.052	0.163
45	28.467	55	28.103	28.377	28.240	0 137
50	28.620	50	28.111	28.410	28.323	0.087

* $T_2 + \frac{(T_1 - T_2)X}{120} = T_4$.

The maximum value of ΔT, and hence $(-\Delta H)$, is at $x = 80$ c.c. (see curve I, Fig. 2).

N.B. Though the absolute values of temperatures shown in this and other tables of this paper are correct only to the tenth of a degree, their relative values amongst themselves are extremely accurate, the accuracy being of the order of one fifth of a small division on a Beckmann thermometer ($\pm$ 0.002°).

TABLE II

Titration of M/5 ammonia soln. with M/10 copper sulphate soln. (Job's method).
(c=0.1. p=2).

M/10-$CuSO_4$ added (100-x) = Xc.c.	M/10-NH_4OH taken in Dewar (x c.c.).	Rise in temp. (ΔT).	M/10-$CuSO$ added (100-x) = X c.c.	M/10-NH_4OH taken in Dewar (x c.c.).	Rise in temp. (ΔT).
5	95	0.101	30	70	0.461
10	90	0.162	35	65	0.453
15	85	0.230	40	60	0.420
20	80	0.322	45	55	0.373
25	75	0.402	50	50	0.316

The maximum value of ΔT lies at x=68 c c., as observed from curve II, Fig. 2.

TABLE III

Titration of M/5 ammonia solution with M/20 copper sulphate solution.
(c=0.05. p=4).

(a) Ammonia soln. taken in the Dewar. (b) Copper sulphate soln. taken in the Dewar.

M/20-$CuSO_4$ added (100−x) =X c.c.	M/5-NH_4OH taken in the Dewar (x c.c.).	Rise in temp. (ΔT).	M/5-NH_4OH added (x c.c.).	M/20-$CuSO_4$ taken in the Dewar (100−x) =X c c.	Rise in temp. (ΔT).
10	90	0.045	50	50	0.260
20	80	0.104	45	55	0.225
30	70	0.167	40	60	0.203
35	65	0 205	55	65	0.156
40	60	0.240			
45	55	0.266			
50	50	0.266			

The maximum value of ΔT lies at x=53 c.c., as observed from curve III, Fig. 2.

Siddhanta's Modification of Job's Method of Continuous Variation

'a' c.c. of an ammonia solution of concentration 'c', taken in the Dewar flask, was subjected to a process of continuous titration with a solution of copper sulphate of strength 'pc'. Both parent solutions were made $M/2$ with respect to ammonium sulphate for reasons already stated. As before, the solutions were kept in the draught-free room for half an hour and the initial temperatures, T_1 and T_2, of the solution in the burette (Beckmann B_I) and that in the Dewar (Beckmann B_{II}) respectively were noted, adopting the same procedure as before. Equal small instalments (δx c.c.) of the burette solution were successively added and the liquid mixture was vigorously stirred each time for exactly two minutes by a stopwatch ; immediately afterwards, the final temperatures T_3 of the liquid mixture were read on the Beckmann B_{II} ; T_3 in each previous addition must necessarily be taken as the initial temperature T_2 for the next addition (vide Table IV). The experiment required about half an hour for completion and the temperature T_1 (Beckmann B_I) was found to change con-

TABLE IV

Titration of 40 c.c. of M/10 ammonia solution taken in the Dewar with M/10 copper sulphate solution (Siddhanta's method).
(a=40 c.c. c=0.1. p=1. δx=1 c.c.)

M/10-$CuSO_4$ solution added. x c.c. ($=\Sigma\delta x$).	Water equivalent of the Dewar. $W=(a+x)/5$.	Temp. of M/10 $CuSO_4$ solution added from burette (as read by Beckmann B_I). T_1	Initial temp of M/10 ammonia solution in the Dewar (as read by Beckmann B_{II}). T_2	Final temp. on mixing (as read by Beckmann B_{II}). T_3	Mean initial temp. of the mixture assuming no reaction to take place (T_4 *.	Temp. change due to reaction for each addition $\delta T=T_3-T_4$.	$\delta(-\Delta H)=(a+x+W)\delta T$.	$(-\Delta H)=\Sigma\delta(-\Delta H)$.	$\frac{(-\Delta H)}{a+x}$.
1	8.2	26.880	27.182	27.218	27.176	0.042	2.07	2.07	0.050
2	8.4	26.903	27.218	27.258	27.212	0.046	2.32	4.39	0.105
3	8.6	26.831	27.258	27.297	27.252	0.045	2.32	6.71	0.156
4	8.8	26.955	27.297	27.332	27.291	0.041	2.17	8.88	0.202
5	9.0	26.980	27.332	27.366	27.325	0.041	2.21	11.09	0.246
6	9.2	27.006	27.366	27.394	27.359	0.035	1.93	13.02	0.283
7	9.4	27.026	27.394	27.418	27.387	0.031	1.75	14.77	0.314
8	9.6	27.047	27.418	27.435	27.411	0.024	1.38	16.15	0.337
9	9.8	27.071	27.435	27.444	27.429	0.015	0.88	17.03	0.348
10	10.0	27.090	27.444	27.450	27.438	0.012	0.72	17.75	0.355
11	10.2	27.106	27.450	27.450	27.444	0.006	0.37	18.12	0.355
12	10.4	27.121	27.450	27.450	27.445	0.005	0.31	18.43	0.354
13	10.6	27.133	27.450	27.449	27.445	0.004	0.25	18.68	0.352
14	10.8	27.146	27.449	27.447	27.444	0.003	0.19	18.87	0.350
15	11.0	27.159	27.447	27.444	27.443	0.001	0.07	18.94	0.344

* $T_4=T_2+\frac{(T_1-T_2)\,\delta x}{a+x+W}$

The value of $[-\Delta H/(a+x)]$ is maximum at x=10 c.c. (vide curve IV, Fig. 3).

tinually during this period, thus necessitating the recording of T_1 during each step of addition (for accuracy, addition and noting the temperature T_1 should be done simultaneously). From the values T_1, T_2 and T_3, thus recorded, the temperature change δT due to the reaction occurring after each step of addition of δx c.c. of the burette solution was then calculated as shown in Table IV. The heat of reaction $\delta(-\Delta H)$ due to each addition (δx c.c.) of the burette solution is then given by

$$\delta(-\Delta H) = (a+x+W)\,\delta T$$

where $x=\Sigma\delta x$ at that stage and W is the water equivalent of the calorimeter to be calculated by the formula, $W=(a+x)/5$ for our particular Dewar, as already explained. The total heat of reaction $(-\Delta H)$ due to addition of x c.c. $(=\Sigma\delta x)$ of the burette solution is evidently given by $(-\Delta H)=\Sigma\delta(-\Delta H)$.

TABLE V

Titration of 40 c.c. of M/5 ammonia solution taken in the Dewar with M/10-copper sulphate solution (Siddhanta's method).
(a = 40 c.c. c = 0.2. p = ½. δx = 2 c.c.).

$x=\Sigma\delta x$.	$a+x$.	$W=(a+x)/5$.	δT.	$\delta(-\Delta H)=\delta T(a+x+W)$.	$(-\Delta H)=\Sigma\delta(-\Delta H)$.	$(-\Delta H)/(a+x)$.
2	42	8.4	0.063	3.18	3.18	0.076
4	44	8.8	0.067	3.54	6.72	0.153
6	46	9.2	0 061	3 37	10.09	0.219
8	48	9.6	0.058	3.34	13.43	0 280
10	50	10.0	0.056	3.36	16.79	0.386
12	52	10 4	0.052	3 25	20 04	0 385
14	54	10.8	0.042	2.72	22.76	0.422
16	56	11.2	0.028	1.88	24.64	0.440
18	58	11.6	0.018	1.25	25.89	0.446
20	60	12.0	0.002	0.14	26.03	0.434
22	62	12.4	−0.002	−0.15	25 88	0.417
24	64	12 8	−0 007	−0.54	25 34	0.396
26	66	13.2	−0.005	−0.40	24.94	0 378
28	68	13.6	−0.005	−0.41	24.53	0.361
30	70	14.0	−0 007	−0.59	23.94	0.342

The maximum value of $[-\Delta H/(a+x)]$ is at $x=19.0$ c.c., as observed from curve V, Fig. 3.

TABLE VI

Titration of 40 c.c. of M/5 ammonia solution taken in the Dewar with M/15-copper sulphate solution (Siddhanta's method).
(a = 40 c.c. c = 0.2. p = 1/3. δx = 3 c.c.).

$x=\Sigma\delta x$.	$a+x$.	$W=(a+x)/5$.	δT.	$\delta(-\Delta H)=\delta T(a+x+W)$.	$(-\Delta H)=\Sigma\delta(-\Delta H)$.	$(-\Delta H)/(a+x)$.
3	43	8.6	0.038	1.96	1 96	0.046
6	46	9.2	0.040	2.21	4.17	0.091
9	49	9.8	0.048	2.82	6 99	0.143
12	52	10 4	0.039	2.43	9.42	0.181
15	55	11.0	0.039	2.57	11.99	0 218
18	58	11.6	0.033	2.30	14.29	0.246
21	61	12.2	0.024	1 76	16.05	0.263
24	64	12.8	0.019	1.46	17.51	0.274
27	67	13.4	0 010	0 80	18.31	0.273
30	70	14.0	−0.003	−0 25	18.06	0 258
33	73	14.6	−0 002	−0.18	17 88	0.245
36	76	15 2	−0.004	−0 36	17.52	0.230
39	79	15 8	−0.005	−0.47	17.05	0.216
42	82	16.4	−0 011	−1.08	15.97	0.195
45	85	17.0	−0.012	−1.22	14 75	0.173

The maximum value of $[-\Delta H/(a+x)]$ lies at $x=27.5$ c.c., as found from curve VI, Fig. 3.

TABLE VII

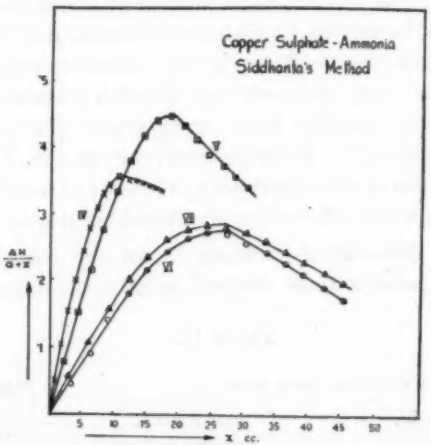
Titration of 30 c.c. of M/5 ammonia solution taken in the Dewar with M/20-copper sulphate solution = (Siddhanta's method).
(a = 30 c.c. c = 0.2, $p = \frac{1}{4}$. δx = 3 c.c.).

$x = \Sigma\delta x$.	$a+x$.	$W=(a+x)/5$.	δT.	$\delta(-\Delta H) = \delta T(a+x+W)$.	$(-\Delta H) = \Sigma\delta T(-\Delta H)$.	$(-\Delta H)/(a+x)$.
3	33	6.6	0.045	1.78	1.78	0.054
6	36	7.2	0.047	2.03	3.81	0.106
9	39	7.8	0.049	2.29	6.10	0.156
12	42	8.4	0.046	2.32	8.42	0.200
15	45	9.0	0.040	2.16	10.58	0.235
18	48	9.6	0.034	1 96	12 54	0.261
21	51	10 2	0.024	1 47	14 01	0.275
24	54	10.8	0 020	1.30	15.31	0 284
27	57	11.4	0.010	0.68	15.09	0.280
30	60	12.0	0.005	0 36	15.35	0.272
33	63	12.6	0.002	0.15	16.50	0.262
36	66	13.2	−0.002	−0.16	16.34	0.247
39	69	13.8	−0.005	−0 41	15.53	0.231
42	72	14.4	−0 005	−0.43	15.50	0.215
45	75	15.0	−0.006	−0.54	14.96	0 200

The maximum value of $[-\Delta H/(a+x)]$ lies at x = 26.5 c c , as found from curve VII, Fig. 3.

In Tables IV—VII are recorded the values of $(-\Delta H)$ and those of $(-\Delta H)/(a+x)$ for the corresponding values of x, taking both equimolecular (Table IV) and non-equimolecular parent solutions (Tables V, VI and VII) The values of $(-\Delta H)/(a+x)$ have been plotted against the corresponding values of x and the resulting curves are shown in Fig. 3 ; curves IV, V, VI and VII correspond to Tables IV, V, VI and VII respectively.

FIG. 3



In the case of equimolecular parent solutions, it is seen from curve IV (a=40 c.c.) that the value of $(-\Delta H)/(a+x)$ is maximum when x = 10 c.c., and hence, the reacting

proportions of ammonia and copper sulphate are in this case given by $m/n = a/x = 4$; m and n refer to the reaction $mA + nB \rightleftharpoons A_mB_n$, where A and B are the reacting molecules (cf. Part II, *loc. cit.*).

The values of x for the maximum points in curves V, VI and VII (parent solutions, non-equimolecular) have been utilised in calculating the dissociation constant K of the cuprammine complex using the formula (6 b), referred to in Part II (*loc. cit.*).

The above formula has been used for evaluating K, since in all the above cases under discussion the values of p are less than unity. The result of the calculations is shown below in a tabular form.

TABLE VIII

Table No.	Curve No.	a.	x at the max. pt.	c.	p.	K (approx.).
V	V	40 c.c.	19 c.c.	0.2	1/2	2×10^{-9} at 28°
VI	VI	40	27.5	0.2	1/3	2×10^{-9} at 28°
VII	VII	30	26.5	0.2	1/4	3×10^{-9} at 30.5°

DISCUSSION

Applying his method of continued variation to the copper nitrate-ammonia system (one of the primary solutions containing ammonium nitrate to prevent the precipitation of basic copper salts) and using molar extinction coefficient as the indicative property, Job (*Ann. chim.*, 1928, *x*, **9**, 186) has found unequivocally one maximum only, corresponding to the complex $Cu(NH_3)_4^{2+}$. The same type of curve, showing only one unequivocal maximum corresponding to the same complex, has also been found in this work, both by the calorimetric adaptation of Job's method and Siddhanta's modified method using molar heat content as the index property. Vosburgh and Coopef (*J. Amer. Chem. Soc.*, 1941, **63**, 437) have developed a method by which the composition of more than one complex formed, by mixing two primary solutions, can be determined by Job's method utilising molar extinction coefficient as the indicative property. Using primary solutions of copper sulphate and ammonia (one of which contained ammonium sulphate dissolved in it), the above workers have demonstrated the existence of complexes $[Cu(NH_3)_4]^{2+}$ and $[Cu(NH_3)_2]^{2+}$. In our opinion, the complex $[Cu(NH_3)_2]^{2+}$, even if formed under the conditions of our experiment, is present in small amounts only so that the effect of its formation is not reflected on our curves (as also on Job's).

The values of the dissociation constant K for the complex $[Cu(NH_3)_4]^{2+}$, as obtained by Job, are compared to those obtained by us in the following table.

TABLE IX

	Job's method using molar extinction (Job).	Job's method using molar heat content (present authors).	Siddhanta's modification using molar heat content (present authors).
K	0.5×10^{-9} at 16°	3.5×10^{-9} at 28-30°	2.4×10^{-9} at 28-30°

The value of K as found by Job is a little lower than our value ; this is evidently in part due to the lower temperature of experiment used by Job. The inherent uncertainty of finding out the value of x for the peak point of the curve (which is rather flat as the peak in all cases) must also be considered; any inaccuracy of locating the peak would lead to the corresponding inacuracy in the value of K, and hence, the latter, determined by Job's method, is approximate and only indicative of the order.

The authors' grateful thanks are due to Prof. Priyadaranjan Rây, Indian Association for the Cultivation of Science, Jadavpur, for his kind interest and guidance. The work was done a few years back, at the Chemical Laboratory, Presidency College, Calcutta and the authors' thanks are also due of Prof. N. K. Sen, Head of the Department of Chemistry, Presidency College, Calcutta for taking interest and providing facilities.

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ON THE ANALYTICAL APPLICATION OF DUTOIT'S THERMO-VOLUMETRY. PART I. ANALYSIS OF CALCIUM AND MAGNESIUM IN DOLOMITE

By Kumar Krishna Chatterji

It has been shown that a volume correction for temperature change is indispensible which eliminates fictitious breaks, often occurring in the thermometric titration curves.

The method has been applied for thermometric estimation of Mg in a solution by titration with standard microcosmic salt and also for the estimation of Ca and Mg in dolomite solution, by titration first with a standard ammonium oxalate solution for Ca, followed by a second titration of the same solution with a standard microcosmic salt solution, under conditions adopted in the quantitative separation of these elements employing the same reagents.

The method of thermovolumetric titration introduced by Dutoit and Grobet (*J. chim. phys.*, 1922, **19**, 324) has been widely employed during recent years for studying the course of various neutralisation, precipitation and complex formation processes in solution. The potentiality of the method, however, as a tool for the quantitative estimation has been little appreciated, as would appear from the rather scanty references in this field of its application, the only references available being the works of Dean *et al.* (*J. Amer. Chem. Soc.*, 1924, **46**, 885 ; 1925, **47**, 64), Mayr and Fisch (*Z. anal. Chem.*, 1929, **76**, 418) and Chatterji (*Science & Culture*, 1949, **14**, 530).

The method, however, suffers from some obvious limitations which must be taken into account where the object is to apply the method for quantitative estimations.

The graphical representation of the course of a thermometric titration consists in plotting the total change in temperature (ΔT in °C) produced in a reaction against the volume of the solution of one of the reactants which is added to a fixed volume (V c.c.) of the second reactant, taken in a Dewar flask. Since the thermometric titration curves are drawn into straight lines, this would suggest, firstly, that the specific heat of the contents of the Dewar flask remains unaltered by the change in its concentration and composition by the addition of the titrant, and secondly, that the temperature change is not affected by dilution, and, for a particular reaction, is the same for addition of every equal volume of the titrant to the solution being titrated.

Granting the first assumption as approximately true for dilute solutions, the fallacy underlying the second one must not be underestimated, since during the titration the volume of the solution in the Dewar flask is often considerably increased by the volume of the titrant added, and the temperature change (ΔT) produced by adding the same volume of the titrant will continuously diminish with the progress of the titration although the heat change (ΔH) at every instalment of the addition of the titrant remains the same.

The change in the value of ΔT is negligible if dilution is small (approxly. within 5%), but for larger dilution, the latter factor will seriously affect the course of the change in temperature—volume of the titrant curve, which for the same reaction will

not be a straight line but will actually be a curve with a large radius of curvature, having its convexity towards the temperature axis.

The slope of such a curve permits one to represent it with a little effort as a pair of straight lines intersecting clearly near about the middle point of the curvature.

The author has found that such fictitious breaks arising from dilution can be easily eliminated if a volume correction for the change in temperature is effected, and the total temperature change for a constant volume of the titrant, $(T-T_0)C_v$, is plotted against the volume of the titrant added:

[Here, $$(T-T_0)\,C_v = \frac{(T-T_0)(V_0+\Delta V)}{V_0}$$

where T_0 = initial temperature and T = temperature recorded by the Beckmann thermometer by adding ΔV c.c. of titrant to V_0 c.c. of the solution originally present in the Dewar].

In the present investigation the author has carried out the thermometric estimation of Mg in solution containing 2.5 g. of NH_4Cl and 10 c.c. of concentrated ammonia per 0.1 g. of Mg, by titration with a standard microcosmic salt solution, over the range $M/10$ to $M/50$ with respect to Mg^{2+} ion

The range of applicability of Mayr's thermometric estimation of Ca (*loc. cit.*) by titration with a standard ammonium oxalate solution has also been checked and has been found to hold good up to $M/30$ with respect to Ca^{2+} ion.

In a solution containing mixtures of Ca and Mg salts, it has been found possible to carry out the estimation of Ca and Mg individually by a thermometric titration of the solution at about p_H 4 (by adding acetic acid in presence of methyl orange indicator) containing the required quantity of NH_4Cl with standard ammonium oxalate for Ca, followed by a second titration of the same solution with a standard microcosmic salt solution after addition of the required quantity of concentrated ammonia.

The estimation of Ca and Mg in dolomite is based exactly on the above principle.

EXPERIMENTAL

Preparation of Reagents.—Two $M/10$ (approx.) solutions of $MgCl_2$ were prepared by dissolving recrystallised Kahlbaum's A.R. $MgCl_2$, 6 H_2O in distilled water. Magnesium was estimated by 8-hydroxyquinoline. The solution employed for individual estimation of Mg thermometrically contains 0.002432 g. of Mg./c.c., the other one containing 0.0024 g. of Mg/c.c. has been used for determining Mg in a mixture by the same method.

A standard $CaCl_2$ solution (approx. $M/10$) was prepared by dissolving E. Merck's A.R. $CaCO_3$ in HCl (conc.) and neutralising it with ammonia. The solution was brought to p_H 4 by adding a few drops of glacial acetic acid in presence of methyl orange indicator and diluted to the required volume with distilled water. Ca was estimated as calcium oxalate monohydrate ; 1 c.c. of the solution contained 0.004036 g. of Ca. This solution was employed for thermometric estimation of Ca with ammonium oxalate.

A 0.4859 N solution of ammonium oxalate was prepared by dissolving Merck's A.R. ammonium oxalate in distilled water and standardising it against $KMnO_4$.

A 0.4889 *M* solution of microcosmic salt solution was prepared by dissolving in distilled water Merck's A. R. sodium ammonium phosphate and estimating the phosphate as magnesium pyrophosphate.

For estimation of dolomite thermometrically the ore (2.5-3 g.) was dissolved in HCl (conc.), diluted, and about 10 g. of NH_4Cl added and then carefully neutralised by ammonia till Fe, Al, Ti etc. were thrown down as precipitates. The solution was filtered and brought to p_H 4 by adding a few drops of glacial acetic acid in presence of methyl orange indicator and made up to 250 c.c. An aliquot of 50 c.c. of this solution was employed for thermometric titration first by standard ammonium oxalate solution for Ca, and then after adding 5 c.c. of concentrated ammonia the same solution was titrated with standard sodium ammonium phosphate for Mg.

The thermometric arrangement and method of titration were the same as that of Dutoit (*loc. cit.*).

Discussion

Figs. 1 and 2 are the thermometric titration curves of $MgCl_2$ and $CaCl_2$ solutions at three different concentrations of each with standard microcosmic salt and ammonium oxalate solution respectively. The corrected volume curves have been drawn side by side with those without corrections to show clearly the improvement achieved by volume correction.

Fig. 1

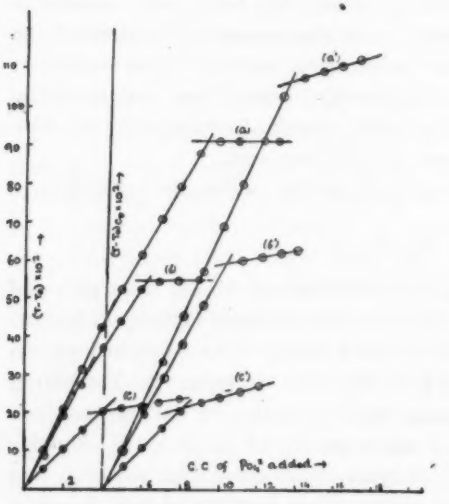
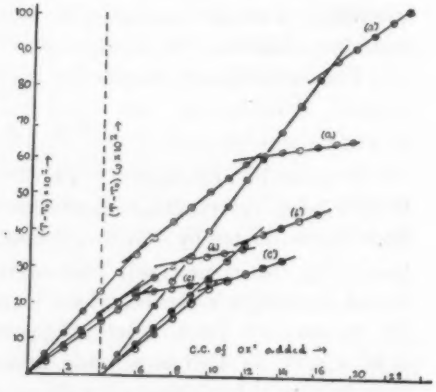


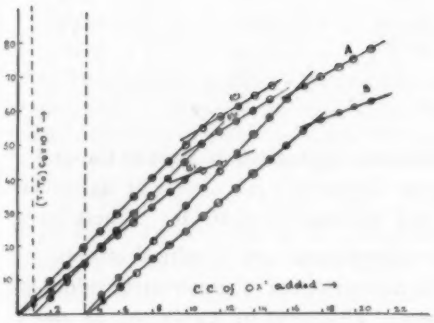
Fig. 2



a,a' :0.1 *M* (45c.c.) $MgCl_2$ *vs.* 0.4889*M* microcosmic. salt. a,a' :0.1*M* (30c.c.) $CaCl_2$ *vs.* 0.4895*M* Am oxalate.
b,b' :0.05 *M* (60 c.c.) ,, ,, ,, ,, b,b' :0.05 *M* (40 c.c.) ,, ,, ,,
c,c :0.02*M* (50 c.c.) ,, 0 2445 *M* ,, ,, c,c' :0.033*M* (45 c.c.) ,, ,, ,,

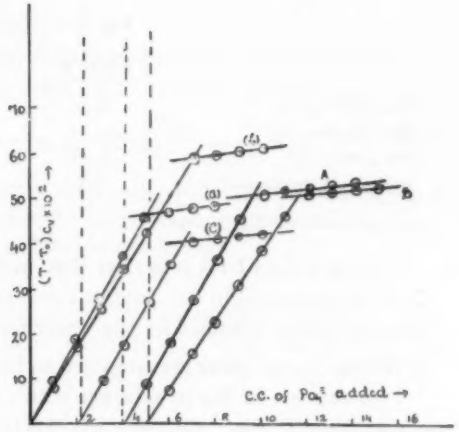
Figs. 3 and 4 represent the $(T-T_0)C_V$ volume of titrant curves for titration of three different mixtures of $CaCl_2$ and $MgCl_2$ solutions and of Ca and Mg in two dolomite samples against standard ammonium oxalate and standard microcosmic salt solutions.

FIG. 3



a: Ca in 0.1*M* of $CaCl_2$ (25cc)+0.1*M*-$MgCl_2$(25c.c.)
b: ,, ,, ,, ,, (35 c.c.)
c: ,, ,, (27 c c.) ,, (22)
A: Ca in dolomite 2
B: ,, ,, ,, 1

FIG. 4



a: Mg in 0.1*M* of $CaCl_2$ (25c.c.)+0 1*M*-$MgCl_2$(25c.c.)
b: ,, ,, ,, ,, (35)
c: ,, ,, (27.5 c.c) ,, (22c c.)
A: Mg in dolomite 2
B: ,, ,, ,, 1

Curves a and b in Figs. 1 and 2 are characterised by two breaks in both cases; while the second break indicates end-point of the reaction, the first break which occurs near the middle point of the curvature arises purely from dilution of the solution and consequent fall in temperature-rise. The effect of volume correction for temperature change is clearly borne out for the same curves a′ and b′ and where $(T - T_o)\,C$ have been plotted against volume of titrant, these and the rest of the curves being perfect straight lines are marked by a single break indicating the end-point of the titration.

TABLE I

	Fig. 1 (Magnesimm)			Fig. 2 (calcium)A		
	Curve a′.	Curve b′.	Curve c′.	Curve a′.	Curve b′.	Curve c′.
End-points (c.c.)	9.3	6 25	4.15	12.45	8.25	6.20
* M (thermo) (in g.)	0.1092	0.0733	0.0243	0.1219	0.0807	0.0606
* M (grav.) (in g.)	0.1094	0.0730	0.0243	0.1211	0.0807	0.0605
% Error in thermometry	0.18	0.5	0.1	0.7	0.05	0.12

TABLE II

	Fig. 3. (Calcium in mixture).			Fig. 4 (Magaesium in mixture).		
	Curve a.	Curve b.	Curve c.	Curve a.	Curve b.	Curve c.
End-point (c.c.)	10.25	10.30	11.35	5.05	7.1	4.50
* M (thermo) (in g.)	0.1003 g.	0.1008	0.111	0.0593	0.083	0.0528
* M (grav.) (in g.)	0.1009	0.1009	0.111	0.06	0.084	0.0530
% Error in thermometry	0.6	0.1	0.1	1.2	0.9	0.45

TABLE III

	Fig. 3. (Ca in dolomite).		Fig. 4. (Mg in dolomite).	
	Curve B.	Curve A.	Curve B	Curve A.
End-point (c.c.)	13.45	12.55	6.55	5.65
* MO (thermo) (%)	29.71	31.18	20 74	20 05
* MO (grav.) %)	29 62	31.08	20.90	20 20
% Error in thermometry	0.3	0.3	0.8	0.7

* M stands for Mg or Ca.

From Tables I-III it is clear that in the individual estimations of Mg and Ca, and of Ca in mixture and in dolomite, the average picture indicates a fair degree of agreement between results obtained by the thermometric and gravimetric methods. Where larger deviations occur, these are supposed to be due to experimental and graphical errors.

In the case of Mg in mixture with Ca and in dolomite, the thermometric values are constantly 1% lower than the gravimetric values. This must be explained as due to slight co-precipitation of magnesium oxalate from the mixture in presence of excess of ammonium oxalate left in the solution after titration of Ca.

The thermometric method of estimation of dolomite is not claimed to excel the chemical methods in accuracy, but in consideration of its simplicity and the quickness with which a pair of thermometric titrations may be done, is recommended as a rapid method for industrial analysis of the ore. The result for Mg must be computed by a correction factor of + 1%.

The author expresses his grateful thanks to Prof. P. B. Sarkar, Ghosh Professor & Head of the Dept. of Chemistry, University College of Science & Technology, Calcutta, for kindly suggesting the problem and providing full facilities for carrying out the work in his laboratory.

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SYNTHESIS IN THE 4-AZAFLUORENE GROUP. PART I. SYNTHESIS OF 4-AZAFLUORENE AND ITS 3-METHYL DERIVATIVE

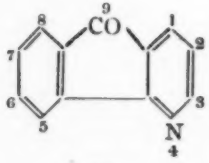
By J. N. Chatterjea and K. Prasad

The azafluorenes named in the title have been synthesised from the related azafluorenones obtained by the cyclisation of appropriate 2-phenylpyridine-3-carboxylic acids. These pyridines were obtained in a few steps from 1 : 3 dicarbonyl derivatives and β-phenyl-β-aminoacrylonitrile.

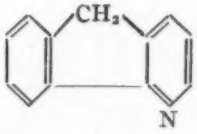
A synthesis of 3-hydroxy- and 3-chloro-4-azafluorene has also been effected.

Petrow *et al.* (*J. Chem. Soc.*, 1949, 2134) have briefly surveyed the work done on synthetic experiments in the 4-azafluorene group (5-indeno [1 : 2-b] pyridine). An admirable account has also been given by Elderfeld and Losin ("Heterocyclic Compounds", Wiley, 1952, Vol. III, p. 342).

Our interest in this field arose from the demonstration by Kruber and Rappen of the existence of 4-azafluorene (II) in coal-tar products (*Chem. Ber.*, 1948, **81**, 483) and the detection of spasmolytic properties in some 2-azafluorenone derivatives (*J. Chem. Soc.*, 1949, 2128). The development of general methods of synthesis of this class of compounds is therefore of great interest and the present paper describes the attainments towards this end.

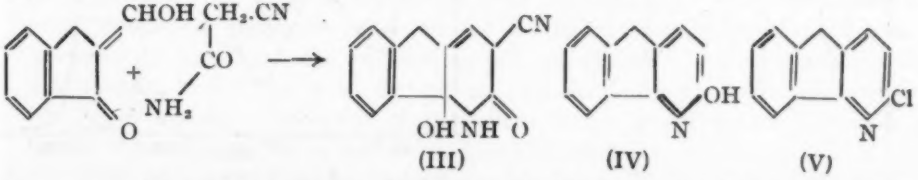


(I)



(II)

The first method we employed started from 2-hydroxymethylene-1-indanone along the lines first developed by Sengupta (*J. Chem. Soc.*, 1915, **107**, 1354) and elaborated extensively by other workers in different fields (von Braun and Lemke, *Annalen*, 1930, **478**, 191 ; Thompson, *J. Amer. Chem. Soc.*, 1931, **53**, 3160 ; Prelog add Geyer, *Helv. Chim. Acta*, 1945, **28**, 1677). The hydroxymethylene compound was conveniently prepared by the improved method of Johnson and co-workers (*J. Amer. Chem. Soc.*, 1944, **66**, 218; 1945, **67**, 1745; cf. Ruhemann and Levy, *J. Chem. Soc.*, 1912, **101**, 2542) by the action of ethyl formate on 1-indanone in the presence of sodium methoxide



(III) (IV) (V)

in benzene. The condensation of this compound with cyanoacetamide proceeded better at higher temperature (50°-52°) than that ordinarily employed (35°-45°). At lower tem-

perature, the reaction was slow with concomitant formation of nitrogen-free substances and other byproducts. The condensation product, 3-keto-2-cyano-4a-hydroxy-2 : 3 : 4 : 4a-tetrahydro-4-azafluorene (III), which was obtained in an optimum yield of 12%, furnished 2-hydroxy-4-azafluorene (IV), isolated as the hydrochloride, on treatment with fuming hydrochloric acid at 170°. The conversion of this hydroxy derivative into the chloro compound (V) presented a difficult problem. For example, the compound is recovered unchanged on refluxing with phosphoryl chloride for 5 hours; the treatment with the same reagent for a short period at 200° in a sealed tube or for a longer period at 170° gave completely decomposed products, whereas at the lower temperature for still longer periods it gave unchanged materials. Success was eventually achieved by employing a mixture of phosphoryl chloride and phosphorus pentachloride under reflux condition for a period of 96 hours, and even then much of the material remained unchanged. The ultraviolet absorption spectrum of the chloro compound (V) is shown in Fig. 1; the nature of the curve and the absorption maxima lie in the same region as that for 4-azafluorene (Fig. 2). Catalytic reduction of this chloro compound with Raney nickel in the presence of sodium ethoxide afforded 4-azafluorene in a very poor yield and in impure condition. Better result was obtained by employing red phosphorus and hydriodic acid, but the paucity of material at our disposal did not permit isolation of

FIG. 1
U.V. spectrum of 3-chloro-4-azafluorene.

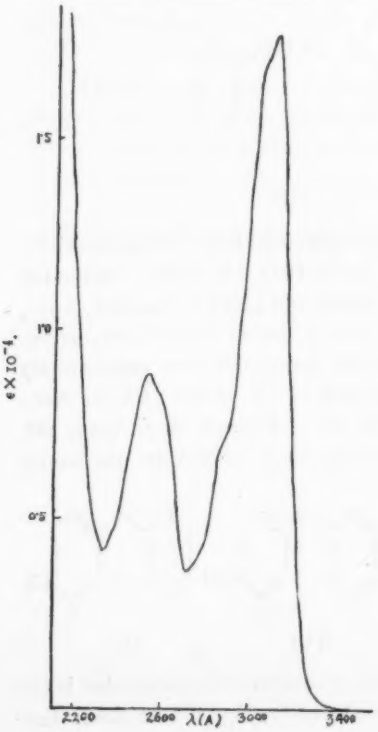
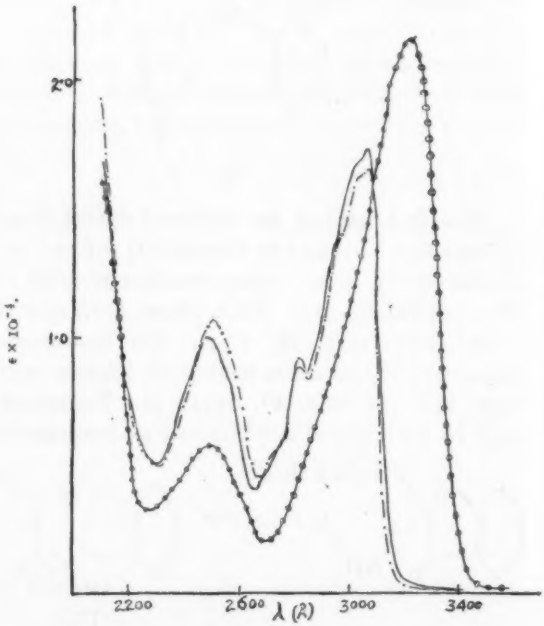


FIG. 2
U.V. spectrum of 4-azafluorene.

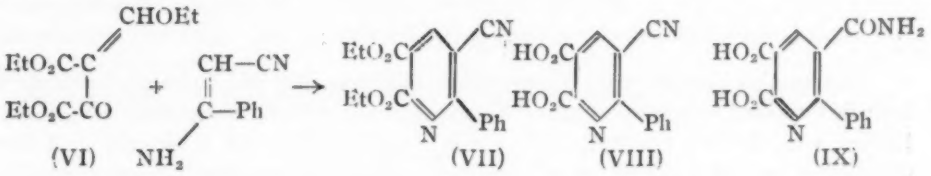


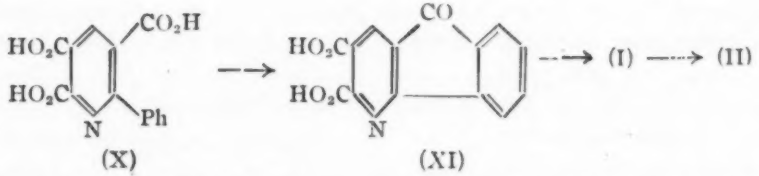
a. In abs. alcohol: —.—.—
b. In p_H 7 (P.B.) :—··—
c. In 0.1-HCl o—o—o—o

4-azafluorene in a pure state, and this necessitated the exploration of alternative routes to this compound.

Claisen (*Annalen*, 1896, **297**, 1) obtained ethyl 2 : 6-dimethyl-3 : 5-pyridine dicarboxylate from ethyl β-aminocrotonate and ethyl ethoxymethylene-acetoacetate. This synthesis has been studied in considerable detail by Jones and his associates culminating in the new elegant synthesis of Vitamin-B_6 (*J. Amer. Chem. Soc.*, 1951, **73**, 4380, 5168, 5244, 5610).

In attempting to apply Claisen's method to the synthesis of azafluorenones we condensed ethyl ethoxymethylene-oxalacetate (VI) (Jones, *ibid.*, 1941, **73**, 3684) with β-phenyl β-aminoacrylonitrile (Holtzwart, *J. prakt. Chem.*, 1889, *i*, **39**, 243) to furnish the cyanopyridine (VII) together with a small quantity of a byproduct, m.p. 225-28°. The condensation was brought about by mere heating the reactants either alone or better in acetic acid ; while none of the expected product was obtained in presence of alcoholic sodium ethoxide.



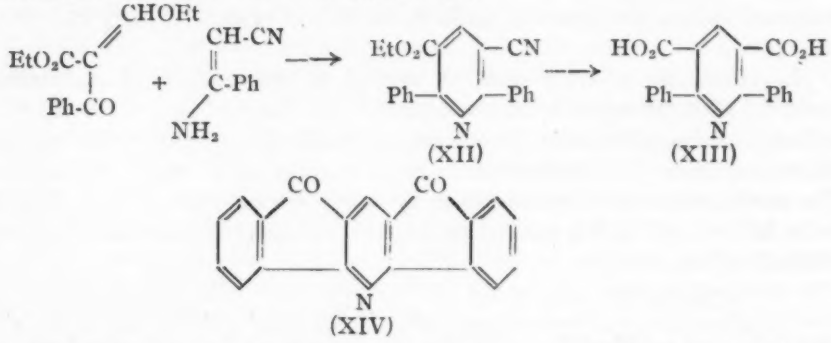


Controlled alkaline hydrolysis of the cyano-ester (VII) gave the cyano-acid (VIII) or the corresponding amide (IX) ; while complete hydrolysis afforded the tricarboxylic acid (X) which on cyclisation through the acid chloride in nitrobenzene yielded the keto-acid (XI).

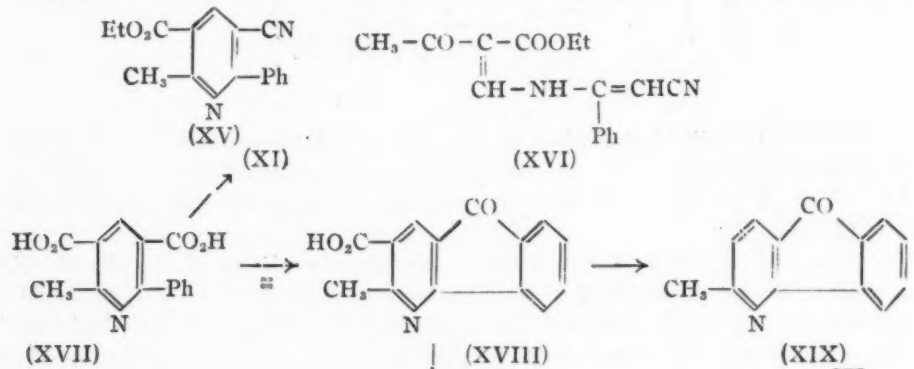
Next our attention was directed to the decarboxylation of the di-acid (XI). Decarboxylation experiments by employing inert solvents, such as liquid paraffin or glycerol, or by heating with soda lime, gave very little, if any, of the desired material (I). On heating (XI) alone above the melting point, a copious sublimate of the unchanged material together with a small quantity of 4-azafluorenone (I) was obtained ; no improvement was noted on admixture with copper-bronze. The best yields have been obtained in small-scale experiments ; scaling up led to catastrophic fall in yields. The synthetic 4-azafluorenone was identical with an authentic specimen prepared from 4-azafluorene, kindly placed at the authors' disposal by Dr. O. Kruber of Gesellschaft für Teerverwertung. Reduction of the ketone with phosphorus and hydriodic acid furnished 4-azafluorene which was identical with the authentic material.

Ethyl ethoxymethylene-benzoylacetate (Weiss and Woidich, *Monatsh.*, 1926, **47**, 427) on similar condensation with β-phenyl-β-aminoacrylonitrile gave the cyano-ester

(XII) which on hydrolysis afforded 2 : 6-diphenylpyridine-3 : 5-dicarboxylic acid (XIII), prepared earlier by Borsche and Hahn (*Annalen*, 1939, **537**, 232) by an altogether different method. This dicarboxylic acid was cyclised by these workers to the azafluorenone (XIV) which was synthesised earlier by Errera by a different method from 1 : 3-diketohydrindene (*Chem Zentrl.*, 1903, II, 950).



The reaction between ethyl ethoxymethylene-acetoacetate and β-phenyl-β-aminoacrylonitrile furnished interesting results. No less than five different compounds were isolated having m.p. 86-88°, 150-52°, 216°, 240-41° and 296-98°. Of these, the first two, obtained in major quantity, were identified respectively as ethyl 3-cyano-2-phenyl-6-methylpyridine-5-carboxylate (XV) and ethyl α-[(2-cyano-1-phenylvinylamino)-methylene]-acetoacetate (XVI) (cf. Jones *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 4381).



Hydrolysis of the former afforded the dicarboxylic acid (XVII). On attempting to cyclise this acid through the acid chloride in nitrobenzene at 60°, the oxidised keto-acid (XI) was obtained, while none of the expected product (XVIII) was detectable. It is

possible that nitrobenzene acted as an oxidising agent. Cyclisation of the acid chloride in cold carbon disulphide, however, afforded the required product (XVIII), whereas the reaction in the same solvent under vigorous conditions gave the oxidised material (XI). The methyl group at the 3-position (azafluorene numbering) is reactive, and therefore it is not extraordinary that it is oxidised so easily. Decarboxylation of the keto-acid (XVIII) by mere heating above the melting point gave much of the unchanged material together with a small quantity of 3-methyl-4-azafluorenone (XI); this was obtained in excellent yield by employing copper-bronze. The synthetic ketone (XIX) and its derivative had the same melting points and properties as described by Errera and Casardi for the same compound synthesised by a long and different route (*Gazzetta*, 1905, **35**, 9). Reduction of the keto-acid (XVIII) by phosphorous and hydriodic acid gave 3-methyl-4-azafluorene-2-carboxylic acid (XX) which on decarboxylation furnished 3-methyl-4 azafluorene (XXI), also obtained by Errera and Casardi by direct reduction of the ketone (XIX).

An attempt to cyclise the open-chain compound (XVI) to the pyridine (XXII) has been so far unsuccessful. By employing sulphuric acid an unidentified byproduct, m.p. 112-13°, has been obtained.

We are engaged in studying other routes to the 4-azafluorene ring system.

EXPERIMENTAL *

3-Keto-2-cyano-4a-hydroxy-2 : 3 : 4 : 4a-tetrahydro-4-azafluorene (III).—2-Hydroxymethylene-1-indanone (4 g., freshly prepared) was added to a solution of cyanoacetamide (2.1 g.) in water (8 c.c.) and just enough alcohol was added to make a homogeneous solution. To this mixture piperidine (0.5 c.c.) was added. The dark mixture was left at 40° till no further solid appeared to separate (72 hours). An orange-coloured nitrogen-free compound (0.01 g.), m.p. 225° (from acetic acid) was separated by filtration. This compound was not investigated further. The filtrate was concentrated at 40° under vacuum, more piperidine (1 c.c.) was added and the mixture left for a further period (72 hours) at 40°. A second crop of crystals (0. 3 g.) which separated was filtered and crystallised in pinkish rectangular plates, m.p. 272-76° from acetic acid. This was again not the desired material. It is probably an intermediate in the formation of the azafluorene. (Found : C, 68.3 ; H, 7.1 ; N, 6.7 per cent). The solution of the compound in acetic acid showed a violet fluorescence. The filtrate was again concentrated, more piperidine (1 c.c.) was added and allowed to remain at 50° for 30 days. A third crop of practically colorless crystals of (III), m.p. 310° (decomp.) after darkening at 250°, was obtained. The compound crystallised from acetic acid in chocolate needles which on drying turned to yellowish matty crystals, m.p. 318-20° (decomp.). (Found : C, 68.9 ; H, 4.4 ; N, 12.6. $C_{13}H_{10}O_2N_2$ requires C, 69.0 ; H, 4.4 ; N, 12.4 per cent).

In a second series of experiments, the reaction mixture was maintained at 50°-55° from the beginning. The nitrogen-free compound that had separated in practically negligible yield during 48 hours was removed and the filtrate concentrated. More piperidine (4-5 c.c.) was added to the mixture which was left at 50°-52° for 24 days.

* All m.p.'s are uncorrected.

The dark brown mass of (III) was filtered which on two crystallisations from acetic acid furnished the cyanoazafluorene (yield 12%), m.p. 318-20° (decomp.).

3-Hydroxy-4-azafluorene (IV).—The foregoing cyano compound (3.6 g.) was heated in a sealed tube with fuming HCl (6 c.c., saturated at 0°-2°) for 15 hours at 170°. The dirty yellow crystals separating were filtered and crystallised from alcohol (containing a few drops of HCl).

The *hydrochloride* of (IV) was obtained in beautiful yellow prismatic needles (2.4 g.), m.p. 302°-306°. (Found : C, 65.6 ; H, 4.8. $C_{12}H_9ON.HCl$ requires C, 65.6 ; H, 4.6 per cent). The compound gave a red ferric reaction.

Free Base.—The hydrochloride (0.05 g.) was suspended in water (5 c.c.) and treated with a moderately strong solution of sodium hydroxide and then heated to boiling. On cooling, colorless silky needles of the *sodium salt* separated from the clear solution. This was collected and on treatment with a large volume of water was immediately hydrolysed to form the free *base* as yellowish needles, m.p. 300°-302°. (Found : C, 78.2 ; H, 5.1. $C_{12}H_9ON$ requires C, 78.7 ; H, 4.9 per cent).

3-Chloro-4-azafluorene (V).—A mixture of the foregoing hydrochloride (1.4 g.), phosphoryl chloride (8 c.c.) and PCl_5 (8.0 g.) was refluxed on a sand-bath for 96 hours. The chlorides of phosphorus were removed in vacuum, the residue treated with ice, the mixture made alkaline with sodium hydroxide and extracted with ether (4 × 20 c.c.). The ethereal extract was dried (potassium carbonate) and the solvent removed to obtain a semi-solid pasty mass (0.25 g.). The alkaline solution on acidification gave unchanged material (0.8 g.) which on repeating the operation furnished a total yield (0.35 g) of the crude *chloro* derivative (V). This was purified by chromatography on an alumina column. On elution with petroleum ether (non-fluorescent band in ultraviolet light),

Fig. 3. I.R spectrum of 4-azafluorene in nujol.

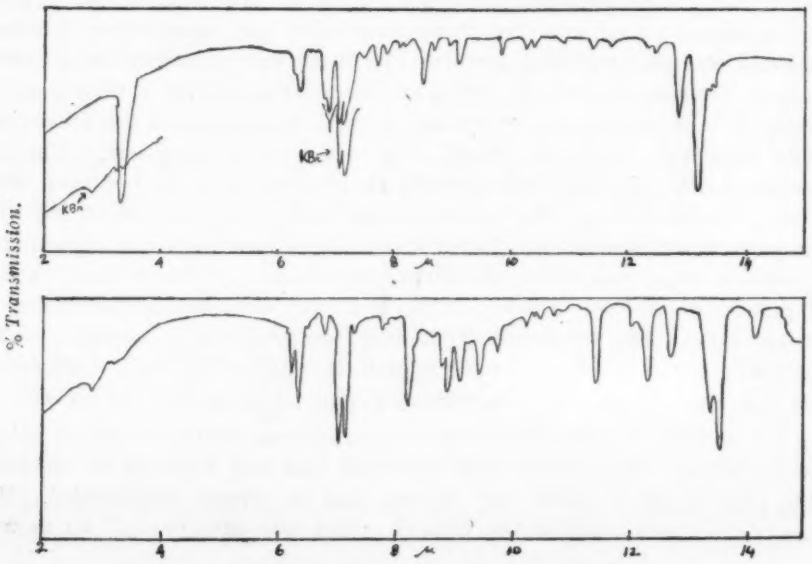


Fig. 4-I.R. spectrum of 3-chloro-4-azafluorene in nujol.

(V) was obtained in colorless prisms after recrystallisation from petroleum ether (30°-60°), m.p. 92-93°, yield 0.13 g. (Found: C, 70.9; H, 4.0. $C_{12}H_8NCl$ requires C, 71.5; H, 3.9 per cent).

Ultraviolet spectrum: λ^{max}_{EtOH}, 2540Å (ϵ=8700); 3110Å (ϵ=18000). *Infra-red spectrum* (Fig. 4): λ^{max}_{nujol}, 6.27 (C = C coniugated) 6.41, 6.81, 7.10, 7.19, 7.82, 8.29 (C—Cl), 8.87, 8.99, 9.16, 9.50, 9.81, 10.32, 10.54, 11.30, 12.40, 12.80, 13.46, 13.61 and 14.22μ.

Reduction of the Chloro Compound (V).—To a solution of NaOEt (0.1g. Na in 5 c.c. of alcohol) the chloro compound (0.1 g.) was added and the material hydrogenated with Raney nickel (0.5 c.c. sediment) at the room temperature and atmospheric pressure. The absorption of hydrogen (*ca.* 15 c.c.) was complete in about 30 minutes. The greenish solution, which was originally bluish, was filtered, alcohol removed on the water-bath and water added when the colour was discharged. This was extracted with ether and dried over potassium carbonate. On removing the solvent, 4-azafluorene was obtained as an oil having a very characteristic odour. The compound did not solidify and its purification could not be undertaken for paucity of the material. A better result was obtained by reducing the chloro compound (6 mg.) with hydriodic acid (0.2 c.c.) and red phosphorus (10 mg.) for 12 hours under reflux. A mixture of crystalline hydriodides of the unchanged chloro compound (major quantity) and 4-azafluorene was obtained. This was collected and basified when the characteristic odour of 4-azafluorene was perceptible, which was isolated by *micro* steam-distillation, followed by extraction with ether, when a trace of an oily material was obtained furnishing a picrate, m.p. *ca.* 200° (lit. m.p. 215°), further purification of which was not possible due to paucity of the material.

Condensation of β-Phenyl-β-aminoacrylonitrile with Ethyl Ethoxymethylene-oxalacetate.—The nitrile (4.8 g.) and ethyl ethoxymethylene-oxalacetate (8 g.) were dissolved in acetic acid (6 c.c.). When all the solid had dissolved, a mild exothermic reaction ensued. On heating for 1½ hours on the water-bath, the mixture gradually darkened and the smell of ethyl acetate became more and more pronounced. After removing the volatile products and acetic acid in vacuum on the water-bath, the residue solidified on keeping overnight. On crystallisation from alcohol, *ethyl 3-cyano-2-phenylpyridine-3:5-dicarboxylate* was obtained as silky needles (5.9 g.), m.p. 92-93°. (Found: C, 66.2; H, 5.0; N, 9.1. $C_{18}H_{16}O_4N_2$ requires C, 66.7; H, 5.0; N, 8.6 per cent). The mother-liquor on keeping furnished a further crop of crystals from which a compound of m.p. 225-28° was isolated, yield 10 mg. The material is sparingly soluble in alcohol. (Found: C, 79.1; H, 4.4 per cent).

2-Phenylpyridine-3:5:6-tricarboxylic Acid.—The foregoing cyano-ester (3.2 g.) was refluxed on the water-bath with NaOH (1.6 g.) in aqueous alcohol (12 c.c., 30%) till the evolution of ammonia had ceased (20-24 hours). The liquid was filtered and acidified with HCl, and on cooling (scratching) silky needles of the *tricarboxylic acid* (2.4 g.) was obtained which were collected, washed with the minimum quantity of water and recrystallised from water in silky needles, m. p. 256-57°, losing water of crystallisation

(forthing) at 153-60°. (Found: N, 4.7. $C_{14}H_9O_6N.H_2O$ requires N, 4.6 per cent). The compound yields a picrate, m.p. 274-76°. On decarboxylation by heating with lime, 2-phenylpyridine was obtained as an oil, affording a crystalline picrate, m.p. 175°.

When the period of hydrolysis was reduced (4-5 hours) and enough absolute alcohol added to the reaction mixture, the *sodium salt* of *3-carbamido-2-phenylpyridine-3 : 5-dicarboxylic acid* was precipitated, which on acidification furnished the related *acid* (IX) as colorless crystals, crystallising from water in prismatic needles, m.p. 295°, losing water of crystallisation at 160°-166°, yield 50%. (Found in the anhydrous material : N, 9.5. $C_{14}H_{10}O_5N_2$ requires N, 9.8 per cent).

The di-ester (VII) on hydrolysis with 2 equivalents of absolute alcoholic potash yielded *3-cyano-2-phenylpyridine-5 : 6-dicarboxylic acid* (VIII) (isolated by way of *potassium salt*), crystallising from water as a colorless mass, m.p. 202-204°, losing water of crystallisation at 152°-156°. (Found : N, 9.9. $C_{14}H_8O_4N_2.H_2O$ requires N, 9.8 per cent).

4-Azafluorenone-2 : 3-dicarboxylic Acid.—2-Phenylpyridine-3 : 5 : 6-tricarboxylic acid (1.5 g.) was refluxed with thionyl chloride (10 c.c.) till all the solid had gone into solution (1½ hours). The residue after removal of thionyl chloride was dissolved in freshly distilled nitrobenzene (25 c.c.), treated in the cold with $AlCl_3$ (3.0 g.), and then maintained at 60° for 4 hours. After leaving the mixture overnight, the complex was decomposed with ice and HCl. Nitrobenzene was removed by steam distillation and the solid product (0.7 g.) was collected and the filtrate concentrated to yield further solid (0.25 g.). Both the portions were combined, dissolved in enough sodium carbonate and filtered. The *di-acid* was obtained on acidification. This was crystallised from water in light yellow rectangular plates (0.8 g.), m.p. 292° (slow evolution of gas) . (Found: C, 62.6 ; H, 2.9; N, 5.3. $C_{14}H_7O_5N$ requires C, 62.5 ; H, 2.6 ; N, 5 2 per cent).

4-Azafluorenone.—The decarboxylation of the above keto-acid was carried out in batches of 50 mg. by heating with a *micro* Bunsen flame and collecting the sublimate on a cold finger. The light yellow product was treated with sodium carbonate to dissolve the unchanged acid (or any anhydride) and the residue crystallised from water and obtained in long flat needles (12 mg.), m.p. 139°, not depressed on admixture with an authentic specimen (*vide infra*) of 4-azafluorenone. (Found : N, 7.7. Calc. for $C_{12}H_7ON$: N, 7.7 per cent).

The recovered acid was decarboxylated again. The ketone is volatile in steam and has sufficient vapour pressure to volatilise away at 100°. It is fairly soluble in alcohol, slightly soluble in water from which it can be extracted with ether. The *picrate* crystallised from alcohol in yellow needles, m.p. 197.5° (lit., m.p. 197°). The *semicarbazone* was prepared in methanol by heating on the water-bath with sodium acetate, and the *semicarbazide* hydrochloride crystallised from alcohol in nearly colorless needles, m.p. 257-58° after losing a gas (solvent ?) at 240-42° (lit., m.p. 258°). The *oxime*, prepared in pyridine, crystallised from alcohol in colorless prisms, m.p. 245-46° (decomp.). (Found: N, 14.2. $C_{13}H_8ON_2$ requires N, 14.3 per cent).

4-Azafluorenone from 4-Azafluorene.—4-Azafluorene (0.1 g.) in acetic acid (4 c.c.) was treated with chromic acid (0.1 g.) in a little water. The chromate of the base separated in orange-coloured plates. The mixture was heated on the water-bath till the

solution turned completely green (6 hours). The mixture was treated with water and the sides of the vessel scratched when a yellow material separated. It was boiled with alcohol for 15 minutes, filtered, cooled and worked up. 4-Azafluorenone was obtained in flat yellow needles, m.p. 139°.

4-Azafluorene.—4-Azafluorenone (0.1 g.) was boiled under reflux for 7 hours with hydriodic acid (5 c.c., *d* 1.7) and red phosphorus (0.2 g.). On cooling, long colorless needles of the *hydriodide* of 4-azafluorene separated. This was collected and dissolved in warm water and the solution made alkaline with sodium hydroxide. Oily drops of 4-azafluorene separated which quickly solidified (yield, quantitative). On crystallisation from pertoleum ether (60°-80°) this was obtained in colorless prisms, m.p. 93° (lit., m.p. 93°), undepressed on admixture with an authentic specimen. (Found: N, 8.5. Calc. for $C_{12}H_9N$: N, 8.4 per cent). pK_b, = 4.1 (in 50% methanol).

Ultraviolet spectrum: (*a*) In absolute ethanol $\lambda_{max.}$ 2510 Å (ϵ = 10450); 2820 Å (ϵ = 9050) and 3065 Å (ϵ = 16300)

(*b*) In p_H 7 (phosphate buffer) $\lambda_{max.}$ 2490Å (ϵ = 9780); 2880Å (ϵ = 8700) and 3060Å (ϵ = 17000).

(*c*) In 0.1*N*-HCl $\lambda_{max.}$ 2500Å (ϵ = 5550) and 3220Å (ϵ = 21300).

Infra-red spectrum (Fig. 3): $\lambda^{max.}_{nujol}$ 3.41 (CH_2 stretching frequency), 6.37, 6.89, 7.07, 7.15, 7.71, 7.88, 8.51 8.70, 9.12 (tertiary nitrogen), 9.85, 10.29, 10.41, 11.40, 11.79, 12.49, 12.90 and 13.23μ.

The picrate has m.p. 215° (lit., m.p. 215°). The compound failed to yield a trinitrobenzene derivative. The *picrolonate* crystallised from *n*-butanol in fine yellow needles, m.p. 243-44° (decomp.).

Condensation of β-Phenyl-β-aminoacrylonitrile with Ethyl Ethoxymethylene-benzoylacetate

Ethyl Ethoxymethylene-benzoylacetate (cf. Weiss and Woidich, *loc. cit.*).—A mixture of ethyl benzoylacetate (5.7 g.), ethyl orthoformate (4.4 g.) and acetic anhydride (6.1 g.) was boiled under mild reflux for 1½ hours. The mixture turned slightly yellow and finally brown and smelled strongly of ethyl acetate. After removing the volatile materials under the water pump, the residue was distilled in vacuum. The ethoxymethylene compound was obtained as a thick viscous oil (2.6 g.), b.p. 190-92°/4 mm.

A mixture of the foregoing ethoxymethylene compound (2.6 g.), β-phenyl-β-aminoacrylonitrile (1.5 g.) and acetic acid (3 c.c.) was heated on the water-bath for 8 hours and then allowed to cool. A small quantity of a yellow crystalline material (*ca.* 6 mg.), m.p. 290-92° (a pyridone ?) was obtained. After removing the volatile materials from the filtrate, the residue was left in contact with alcohol (15 c.c.). A crop of crystals of m.p. 140° (clearing at 180°), was deposited and a further amount obtained on concentration of the filtrate. On fractional crystallisation this mixture afforded *ethyl 3-cyano-2:6-diphenylpyridine-5-carboxylate* (XII), m.p. 145°. (Found: N, 8.6. $C_{21}H_{16}O_2N_2$ requires N, 8.5 per cent).

Hydrolysis.—The cyano-ester (0.2 g.) was hydrolysed by refluxing with aqueous alcoholic sodium hydroxide (3 c.c., 40%) for about 20 hours till the evolution of ammonia had ceased. The reaction mixture was filtered and acidified when 2:6-diphenyl-

pyridine-3 : 5-dicarboxylic acid (0.15 g.) was obtained, crystallising from aqueous alcohol in yellowish prisms, m.p. 283° (lit., m.p. 283°). The identity was confirmed by decarboxylating the acid with the aid of a trace of copper-bronze when 2 : 6-diphenylpyridine was obtained, crystallising from alcohol in colorless needles, m.p. 82°.

Condensation of Ethyl Ethoxymethylene-acetoacetate with β-Phenyl-β-aminoacrylonitrile

The nitrile (8 g.) was added to a solution of ethyl ethoxymethylene-acetoacetate (10.3 g., prepared according to Claisen, *loc. cit.*) in acetic acid (10 c.c.). There was no perceptible exothermic reaction. The mixture was heated on the water-bath for 3½ hours and the volatile products removed in vacuum on the water-bath. The last portion of the distillate contained some ethyl acetoacetate. The viscous residue was warmed with alcohol (50 c.c.) and kept overnight in a refrigerator. The crystals separating were filtered and washed with a small quantity of alcohol. The residue (A) and the filtrate (B were separately worked up as follows to yield five different products.

The residue (A) was boiled with petroleum ether (60°-80°) and filtered hot. The filtrate deposited a crop of *ethyl 3-cyano-2-phenyl-6-methylpyridine-5-carboxylate* (XV) (2.8 g.) as long yellowish rectangular plates, m.p. 86-88°. (Found : C, 72.4 ; H, 5.4 ; N, 10.5. $C_{16}H_{14}O_2N_2$ requires C, 72.2 ; H, 5.3 ; N, 10.5 per cent). A second crop (0.5 g.) was obtained by concentrating the mother-liquor. The insoluble residue crystallised from alcohol in light yellow short rhombs (0.43 g.), m.p. 150-52° and proved to be *ethyl α-[(2-cyano-1-phenylvinylamino)-methylene]-acetoacetate* (XVI). (Found : N, 9.9. $C_{16}H_{16}O_3N_2$ requires N, 9.9 per cent). The compound is sparingly soluble in petroleum ether.

The filtrate (B) was concentrated and on keeping in the refrigerator yielded a crop of crystals (filtrate C) which on extraction with pertoleum ether afforded a further crop of the cyano-pyridine (XV) (0.5 g.), m.p. 87.5°. The residue crystallised from alcohol in wooly needles (0.06 g.). m.p. 240-41° (decomp.). (Found : C, 66.6 ; H, 4.7 per cent).

The filtrate (C) on keeping for a few days yielded another crop of crystals which proved to be a mixture, separable on fractional crystallisation from alcohol into the sparingly soluble fraction, m.p. 296-98°. (Found : C, 79.8 ; H, 4.7 per cent) and a mass of colorless felted needles, m.p. 216° (0.04 g.). (Found : C, 67.1; H, 5.9 per cent).

Hydrolysis of the Cyano-ester (XV).—The cyano-ester (2.7 g.) was hydrolysed by boiling under reflux for 20 hours with NaOH (1.0 g.) in water (6 c.c.) and alcohol (3 c.c.). The *acid* crystallised from water in yellowish prisms, m.p. 211-12°, losing water of crystallisation at 134°-140° ; yield 2.2 g. (Found : C, 58.0 ; H, 4.8 ; N, 4.8. $C_{14}H_{11}O_4N$. 2 H_2O requires C, 57.3 ; H, 5.1 ; N, 4.8 per cent). On decarboxylation, 2-methyl-6-phenylpyridine was obtained as a colorless oil, yielding a picrate, obtained in light yellow plates, m.p. 133-34° (lit., m.p. 135°).

Cyclisation of the Acid (XVII).—Cyclisation of the acid (1.5 g.) to the related ketone by way of the acid chloride was attempted in nitrobenzene as in the previous case. On removing nitrobenzene in a current of steam, a dark red residue was left. This was filtered and the aqueous solution on concentration yielded a yellow product

(0.18 g.), m.p. 290-92° and identified as 4-azafluorenone-2 : 3-dicarboxylic acid by direct comparison and by mixed melting point with the authentic specimen described before. (Found : C, 61.9 ; H, 2.9. Calc. for $C_{14}H_7O_5N$: C, 62.5 ; H, 2.6 per cent). The identity was further confirmed by decarboxylating the acid to 4-azafluorenone. Both the specimens gave on heating with resorcinol and a few drops of H_2SO_4, followed by basification with alkali, a red solution which on dilution with water exhibited a green fluorescence, very similar to fluorescein, but much less pronounced. The residue, mentioned above, on working up gave a further yield (0.1 g.) of the same oxidised material. The normal cyclised product was obtained by the following method : The acid (2.0 g.) was suspended in dry chloroform (30-40 c.c.) and converted into the acid chloride by refluxing with PCl_5 (7 g.) till all the material went into solution (15 minutes). Chloroform and chlorides of phosphorus were removed in vacuum, the last traces being removed by repeated addition and subsequent removal of CS_2. The cooled solution of the syrupy residue in dry CS_2 (40 c.c.) was treated with $AlCl_3$ (6.0 g.) in small portions and then left overnight at the ordinary temperature. Next day, CS_2 was removed by decantion, the Al-complex decomposed with ice and HCl and traces of CS_2 removed in a current of steam. A solid residue, left behind, was dissolved in sodium carbonate, clarified by animal charcoal, and acidified to give the *acid* (XVIII) (0.7 g.), crystallising from water in light yellow, wooly mass, m.p. 248-49° with slight previous sintering probably due to decarboxylation. (Found : C, 69.9 ; H, 3.7 ; N, 5.8. $C_{14}H_9O_3N$ requires C, 70.2 ; H, 3.8 ; N, 5.9 per cent). The acid (XVII) could not, however, be cyclised with either H_2SO_4 or polyphosphoric acid.

Decarboxylation of the Keto-acid.—The keto-acid (0.2 g.) was mixed intimately with copper-bronze and distilled cautiously to afford 3-methyl-4-azafluorenone as a yellow oil which solidified quickly. Crystallised from light petroleum, this was obtained in light yellow needles, m.p. 120-21° (lit., m.p. 121°). (Found : N, 7.9. Calc. for $C_{13}H_9ON$: N, 7.2 per cent). The identity was confirmed by the preparation of the oxime (by the pyridine method), m.p. 256-57° (Errera and Casardi report m.p. 256-57°).

Reduction of the Keto-acid (XVIII).—A mixture of the keto-acid (0.4 g.), HI (12 c.c., *d* 1.7) and red phosphorus (0.5 g.) was refluxed for 7 hours. The mixture was diluted, boiled, filtered and on concentration on the water-bath, yellowish prisms of the *hydriodide* of *3-methyl-4-azafluorene-2-carboxylic acid* appeared. These were collected and the free *base* liberated with the aid of sodium acetate. The acid crystallised from water in nearly colorless needles (0.2 g.), m.p. 260-62°. (Found : N, 6.4. $C_{14}H_{11}O_2N$ requires N, 6.2 per cent).

The base on decarboxylation with the aid of copper-bronze furnished 3-methyl 4-azafluorene as a light yellow oil having a similar but less pronounced odour as 4-azafluorene. On leaving in contact with water in the refrigerator, the hydrate was obtained as a crystalline mass melting to an opaque liquid at 47-48° clearing (with the evolution of water vapour) at 100° (cf. Errera and Casardi, *loc. cit.*). The picrate was obtained in yellow needles, m.p. 211° (lit., m.p. 211-12°). The *picrolonate* crystallised from alcohol in yellow prismatic mass, m.p. 252-54° (decomp.).

Cyclisation of the Open-chain Compound (XVI).—The compound (0.35 g.) was added in small portions to cooled sulphuric acid (2 c.c.) when an exothermic reaction

took place. After 2½ hours, the yellowish mixture was added to ice and the precipitated material (0.2 g) filtered. This was crystallised from water yielding a crop of crystals in colorless flat needles, m.p. 112-13°, evolving a gas above 170°. (Found : C, 66.5 ; H, 6.0 ; N, 7.8 per cent). The compound gave off ammonia on heating with alkali. Exhaustive attempts on cyclisation could not be undertaken due to shortage of material.

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THE TEMPERATURE COEFFICIENT OF THE SILVER ELECTRODE POTENTIAL IN SOLUTIONS INITIALLY FREE FROM THE METAL IONS

By H. Khalifa and I. M. Issa

The potentials set by the silver electrode in universal buffer solutions are found to be less positive by ~ 0.7 volt than the thermodynamic E'_o value of the silver-silver oxide system. The temperature coefficient of the massive silver electrode potential, as measured between 15° and 55°, is found to be high and variable, and thus not corresponding to that of stable systems.

In a previous investigation (this *Journal*, 1954, **31**, 426) we applied the silver electrode as an indicator electrode in acid-base titrations. This was based on the fact that the potentials set by silver electrodes of different types showed linear variation with change of p_H (Tourky and Issa, unpublished work). By titrating the universal buffer mixture of Britton and Robinson ("Hydrogen Ions", Vol. I, 3rd Ed., pp. 312, 322) with alkali hydroxide, using the silver electrode as indicator for hydrogen ions, linear potential p_H plots were obtained with $\Delta E/\Delta p_H = 21.5$ mv (Khalfa and Issa, *loc. cit.*). By extrapolating the curves to zero p_H an E'_o value amounting to ~ 0.4 volt more positive than the hydrogen electrode potential is obtained. By comparing this value with the standard potential of the silver-silver oxide system amounting to 1.17 volt, it is apparent that the silver electrode does not behave under these conditions as a metal-metal oxide electrode.

This confirms the previous observations of Kreuger and Kahlenberg (cf. Gatty and Spooner, "The Electrode Potential Behaviour of Corroding Metals in Aqueous Solution", 1938, p. 169) and Gatty and Spooner (*loc. cit.*, pp. 163, 169) who found also that bubbling oxygen caused the potentials to become less positive. However, on addition of silver oxide to the electrode system, the potential became that of the silver-silver oxide couple.

In order to throw some light on the observed phenomena, we studied the effect of temperature on the electrode potentials set by silver electrodes on titrating the universal buffer mixture with alkali hydroxide. This method was followed because it yielded more regular variation of potential with p_H than the potentials measured in unstirred buffer solutions of varying p_H (Tourky and Issa, *loc. cit.*), thus facilitating the process of extrapolation.

The theory underlying this idea is that the temperature coefficient of stable systems such as Ag/Ag^+ (Lingane and Larson, *J. Amer. Chem. Soc.*, 1937, **59**, 2271) or the Cu/Cu_2O (Tourky and Khairy, *J. Chem. Soc.*, 1952, 2626) are but small amounting to ~1 mv/°C, whereas that of unstable systems is always high and variable (Tourky and Khairy, *loc. cit.*).

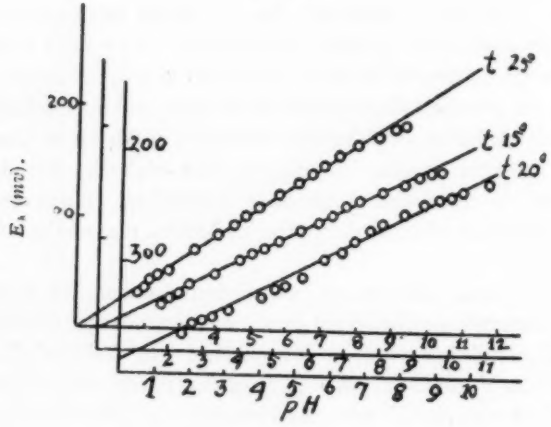
Experimental

The electrodes used in this investigation were of the massive type consisting of spectroscopically pure silver rods of 3 cm. in length and 0.8 mm. in diameter, provided by Johnson Matthey, England. These were fitted to glass tubings with sealing wax.

Electrical contact was maintained through copper wires soldered to the inner end of the silver rod. The electrodes were always polished with fine emery paper before each experiment and washed with the universal buffer mixture before immersion. They were then left in contact with the solution, before the first alkali addition, for a period of one hour which was found sufficient for both thermal and electrical equilibria to be attained. During measurements only half of the electrode was immersed in the solution in order to prevent the latter from coming in contact with the sealing wax.

The potentials were measured at temperatures ranging from 15° to 55°. The titration vessel used was a 400 ml. pyrex glass beaker, fitted with a rubber stopper furnished with the necessary holes for two silver electrodes, a potassium nitrate salt bridge, a glass stirrer, and an inlet for the tip of the burette. The beaker was dipped in a water thermostat, the temperature of which was kept constant throughout the whole process. The alkali hydroxide was added in portions of 2 ml. each from a calibrated burette, fed from a special device which did not allow the solution to come in contact with atmospheric carbon dioxide. The p_H values of the universal buffer mixture at each alkali addition were determined in separate titrations by using a hydrogen electrode of the Hildebrand type as an indicator electrode in conjunction with a saturated calomel electrode as the other half cell.

FIG. 1



The potentials set at each temperature were plotted against p_H, as shown in Figs. 1 to 3. By extrapolating the linear portions of these curves to zero p_H, E'_0 values, as recorded in Table I, were obtained. On plotting these E'_0 values against temperature, the E'_0-temperature diagram (Fig. 4) was obtained.

TABLE I

Temp.	15°	20°	25°	30°	35°	40°	45°	50°	55°
E'_0 (mv)	380	388	400	384	360	390	400	374	368

Evaluation of the Standard Electrode Potential of the Ag/Ag_2O *System.*—The E_o' value of the Ag/Ag_2O system can be calculated from the relations:

$$E = E_o + RT/F \log [Ag^+]$$

For a silver electrode in contact with its oxide, the metal ion activity is equal to that produced by the dissociation of the oxide, and hence,

$$E = E_o + RT/F \log s/[OH^-]$$

where s is the solubility product of AgOH. Substituting for $[OH^-]$ by $K_w / [H^+]$

$$E = E_o + RT/F \log s/K_w + RT/F \log [H^+].$$

Taking $s = 1.78 \times 10^{-8}$ [Gatty and Spooner, *loc. cit.*), $K_w = 1.0083 \times 10^{-14}$ (Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194), $E_o = 0.7991$ volt (Latimer, 'Oxidation Potentials", Prentice Hall, New York, 1953, p. 191) and $RT/F = 0.0591$, all at 25°,

$$E = 0.7991 + 3692 - 0.0591\ p_H.$$

On extrapolation to zero p_H it follows that $E'_o = 1.1683$ volt at 25°, which coincides with the value 1.17, obtained by Luther and Pokorny (*Z. anorg. Chem*, 1908, **57**, 290).

FIG. 2

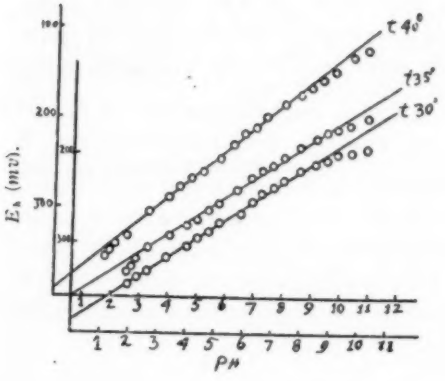
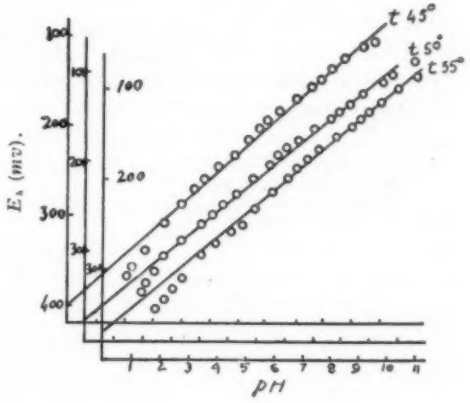


FIG. 3



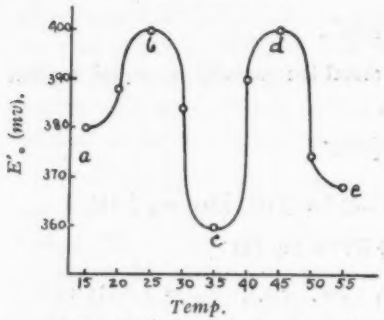
From the data and the corresponding figures it is apparent that at no temperature does the E'_o value approach the standard silver-silver oxide potential. It is also apparent that the E'_o-temperature diagram (Fig. 4) is characterised by minima and maxima within the temperature range used. The temperature coefficients, as calculated from the different parts of the undulatory curve, are shown in Table II.

TABLE II

Portion of curve	a–b.	b–c.	c–d.	d–e.
Temp. coeff. (mv/1°)	+2	−4	+4	−3

The values indicate that the temperature coefficient is high and variable, and cannot thus be considered to correspond to a stable system. In this latter case the temperature coefficient amounts to ~ 1 mv/1°. Undoubtedly the potentials set are more negative than the value of the Ag/Ag_2O system by ~ 0.7 volt, and accordingly, they do not correspond to those of the silver-silver oxide couple. This may find its origin in the fact that silver being a noble metal does not easily oxidise when exposed to atmospheric oxygen and/or does not dissolve in solution to yield silver ions sufficient to saturate the solution with Ag_2O with subsequent deposition of the oxide on the metal surface. Working with highly purified silver oxide, however, Buehrer (cf. Lewis and Randall, "Thermodynamics," 1923, p. 483) obtained variable results which were lower than the thermodynamic values. In interpretting these low values Buehrer supposed that they had their origin in the presence of silver suboxide, Ag_4O. Although Levi and Quilco (*Gazzetta*, 1924, **54**, 598) have found no experimental verification concerning the occurrence of Ag_4O, Hickling (*Trans. Faraday Soc.*, 1945, **41**, 337) in studying the anodic behaviour of silver, using the cathode ray oscillograph, observed a small break which he attributed to the possible formation of the suboxide. However, Ag_4O is unstable and no thermodynamic data are available concerning that oxide which make possible the evaluation of the Ag/Ag_4O couple.

FIG. 4



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ON THE DISTRIBUTION COEFFICIENT OF OXALIC ACID BETWEEN ETHER AND WATER

By Prasad Kumar Bhattacharyya

The accepted value of the distribution coefficient of oxalic acid between ether and water as determined by Chandler, is found to diminish with lowering of concentrations when accurate degree of dissociation of the acid is used. The same has now been determined at higher concentrations with appropriate correction at two different temperatures.

This investigation arose out of an enquiry made about the partition coefficient (P) of oxalic acid between ether and water in connection with a routine experiment in this laboratory. The generally accepted value for this coefficient is that due to Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 694).

In calculating P, the appreciable dissociation of oxalic acid in the aqueous layer was considered, and the necessary correction made. When Chandler performed these experiments, the accepted value of the dissociation constant of oxalic acid was $K_a = 3.8 \times 10^{-2}$ at 25°, and the concentrations of undissociated oxalic acid molecules were calculated from this value. The values of P obtained by him were fairly constant.

Since then quite a number of papers have appeared on the more accurate determinations of dissociation constant of oxalic acid (Drucker, *Z. Elektrochem.*, 1920, **26**, 364; Darken, *J. Amer. Chem. Soc.*, 1941, **63**, 1007; Parton *et al.*, *Trans. Faraday Soc.*, 1939, **35**, 542; Cane and Ingold, *J. Chem. Soc.*, 1931, 2156, *et seq*).

Of these the value given by Darken (5.36×10^{-2}) is probably more accurate. If this value of K_a be accepted and applied on the results of Chandler's experiments, the constancy of P deteriorates, specially at low concentrations. This is quite probable as in dilute states the second dissociation becomes appreciable. The values calculated from Chandler's data are recorded in Table I.

Table I

Temp. = 25°

Initial conc. (M)	0.38	0.27	0.22	0.19	0.03	0.08	0.019	0.01	0.0054
$P(K_a = 3.8 \times 10^{-2})$	8.87	8.84	8.81	8.83	8.66	8.64	8.85	8.35	8.5
$P(K_a = 5.36 \times 10^{-2})$	8.03	8.08	7.87	7.84	7.2	7.3	7.2	7.3	7.0

Quite a large number of experiments conducted in this laboratory, more or less, showed the variation of P at low concentrations, as obtained in Chandler's experiments. It is therefore desirable that a more accurate value for P should be available at relatively high concentrations.

To ascertain this, several experiments on the distribution of oxalic acid between distilled water and redistilled ether were carried out at two different temperatures. The value of P is sensitive to the purity of the solvent. Stoppered pyrex bottles containing different amounts of oxalic acid in mixtures of 50 c.c. water and 200 c.c. ether were shaken for several hours and left in constant temperature baths for two days before titration. The concentrations of undissociated acid were calculated by determining α from $K_a = 5.36 \times 10^{-2}$ (25°). The values of K_a at other temperatures were calculated from its known average temperature coefficient and also from conductivity data (*Amer. Chem. J.*, 1910, **43**, 87). Some of the typical values of P, determined as such, are shown in Table II. The entire amount of oxalic acid in ether layer is assumed to be single undissociated molecules.

TABLE II

K_a (25°) $= 5.36 \times 10^{-2}$. K_a(34°-35°) $= 4.7 \times 10^{-2}$.

Initial conc. (N):	1.5	1.25	1.00	0.5	0.44	0.40
			Temperature = 25°.			
Conc. in aq. layer :	0.57	0.48	0.38	0.195	...	0.16
$P = \frac{C(1-\alpha)}{C_{ether}}$:	10.49	10.54	10.49	10.5	...	10.54
			Temperature = 34-35°.			
Conc. in aq layer:	0.523	0.439	0.353	0.180	0.160	0.143
$P = \frac{C(1-\alpha)}{C_{ether}}$:	8.91	9.06	9.03	9.2	9.18	9.18

The distribution coefficient P of oxalic acid between water and ether is thus 10.5 at 25°, a value which is slightly higher than that of Chandler's.

The author expresses his sincere thanks to Prof. P.C. Rakshit for his advice to undertake the work and helping him with necessary guidance and criticism.

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FORMATION OF COMPLEX COMPOUNDS BETWEEN ALKALINE EARTH CHLORIDES AND POTASSIUM CHLORIDE. PART III. SYSTEM-KCl-$CaCl_2$-H_2O. VISCOSITY AND CONDUCTIVITY

By P. C. Bose and L. N. Srivastava

Following the monovariation method, viscosities and conductivities of a series of mixed solutions of KCl and $CaCl_2$ indicate the existence of the following complex compounds: $2KCl.CaCl_2$; $3KCl.2CaCl_2$; KCl. $CaCl_2$; $3KCl\ 4CaCl_2$; $2KCl.\ 3CaCl_2$ and KCl. $2CaCl_2$

Potassium chloride and calcium chloride are known to form double salts. Only three compounds, $KCl.CaCl_2$, $2KCl.3CaCl_2$ and $2KCl.CaCl_2$ are reported to exist in the fused state.

FIG. 1

Conductivity of the system KCl-$CaCl_2$-H_2O.

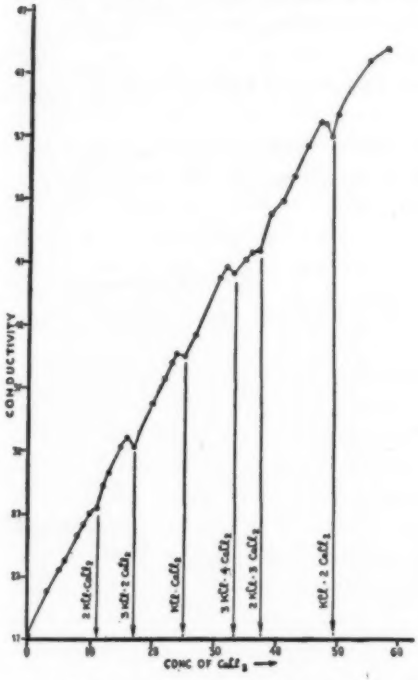
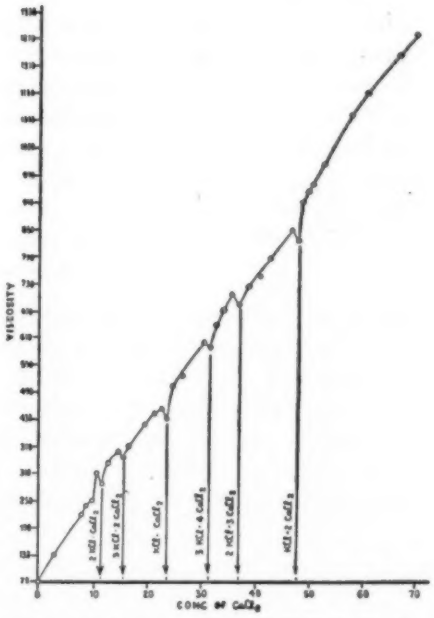


FIG. 2

Viscosity of the system KCl-$CaCl_2$-H_2O.



Menge (*Z. anorg. Chem.*, 1911, **72**, 162) has reported that a compound $KCl.CaCl_2$ is formed (m.p. 754°). Lantsberry and Page (*J. Soc. Chem. Ind.*, 1920, **39**, 37T) have observed from the freezing point curves, the formation of a compound $2KCl.3CaCl_2$. Sato and Amano (*Kinz. No. Kenk.*, 1934, **11**,549) have deduced from the thermal analysis of binary mixtures of KCl and $CaCl_2$ the formation of a compound $CaCl_2.KCl$.

Lightfoot and Prutton (*J. Amer. Chem. Soc.*, 1947, **69**, 2098) have deduced from the isotherm for the ternary system $CaCl_2$-KCl-H_2O the existence of a new compound $2KCl.CaCl_2.H_2O$.

As no systematic work has been done on this system, the authors have undertaken a thorough investigation of the same.

EXPERIMENTAL

The method of monovariation was adopted for preparing the mixed solutions (cf. Part I; this *Journal*, 1953, **30**, 411).

The densities of these solutions were determined by the pyknometer method and the viscosity, by means of an Ostwald viscometer. Conductivities of these solutions were determined by Kohlrausch's method. A conductivity cell, made of pyrex glass having a high cell constant, was used for the purpose. All the usual precautions were taken.

On plotting the values of viscosity and conductivity against the concentration of calcium chloride, the graphs (Figs. 1 and 2) point out six kinks corresponding to 12, 16, 24, 32, 36 and 48 c.c. of KCl, indicating the formation of the following complex compounds: $2KCl.CaCl_2$, $3KCl.2CaCl_2$, $KCl.CaCl_2$, $3KCl.4CaCl_2$, $2KCl.3CaCl_2$ and $KCl.2CaCl_2$. The compounds $3KCl.4CaCl_2$, $3KCl.2CaCl_2$ and $KCl.2CaCl_2$ have so far not been reported by any previous workers.

The authors are grateful to Dr. A.C. Chatterji, Professor of Chemistry for providing the necessary facilities and to late Sri M.R. Nayar, Reader in Chemistry for his kind interest in the work and helpful suggestions.

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KINETICS OF DECOMPOSITION OF PEROXIDES IN SOLVENTS. PART I. CINNAMOYL PEROXIDE

By U. S. Nandi, (late) N. G. Saha and Santi R. Palit

The decomposition of cinnamoyl peroxide has been carried out in different solvents at 60° and 80°. The overall decomposition rate of the peroxide is much higher than that for benzoyl peroxide. The higher rate of decomposition has been ascribed to a higher rate for the induced decomposition of the peroxide.

The true decomposition rate 'k' is more or less higher in case of cinnamoyl peroxide as compared to that for benzoyl peroxide, but values for 'k_i' in case of the two peroxides vary widely. The energy of activation of 26.5 and 24.0 k cals. for 'k' and 26.7 and 22.9 k cals. for 'k_i' have been obtained for cinnamoyl peroxide in ethyl acetate and toluene respectively.

The decomposition of peroxides in solution is complex since reactions with solvent molecules are involved. Early researches were mainly concerned with the identification of the decomposition products. Hey and Waters (*Chem. Rev.*, 1937, **21**, 169) explained this decomposition of peroxides in terms of free radical reaction, which was later on confirmed by other workers. The rate of decomposition of benzoyl peroxide in different solvents has been studied by a number of workers (Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299; Cass, *ibid.*, 1946, **68**, 1976; Barnett and Vaughan, *J Phys. Coll. Chem.*, 1947, **51**, 926, 942), and Nozaki and Bartlett deserve the credit for the first clear formulation of the kinetics of the reaction.

Apart from this, the study of the decomposition of other peroxides (Cass, *J. Amer. Chem. Soc.*, 1950, **72**, 4915; Leffler, *ibid.*, 1950, **72**, 67; Redington, *J. Polymer Sci.*, 1948, **8**, 509) has also attracted much attention in recent literature. The study of aliphatic diacyl peroxides is of interest since their structure and conjugated bonds greatly affect their participation in the radical-induced decomposition reaction. Cinnamoyl peroxide, though similar to benzoyl peroxide, has the special feature that an ethylenic double bond is interposed between the phenyl group and the reactive peroxide linkage, which has led us to study its decomposition.

Experimental

Cinnamoyl peroxide was prepared from the chloride by oxidation with hydrogen peroxide. Cinnamoyl chloride (10 g.) was taken in $CHCl_3$ (10 c.c.) and kept at 0°. To this was added a mixture of H_2O_2 (20 c.c. of 20 volume) and NaOH (6.5 c.c. of 20%),

cooled previously to 0°. The peroxide formed was precipitated a number of times from chloroform solution with methyl alcohol, and was finally dried in vacuo. The peroxide assayed near about 98 to 99%.

Solvents of available high quality were purified and dried by the usual method and finally distilled in an all-glass set.

Procedure.—Pyrex glass ampoules of 5 c.c. capacity were used for the decomposition experiment. These were thoroughly cleaned with chromic acid, washed with water, followed by H_2SO_3 solution, and finally washed with water and dried. Peroxide solution (2 c.c.) was taken in each of the ampoules, frozen in liquid oxygen and sealed in vacuo. These were then kept in an oil thermostat maintained at the required temperature within an accuracy of ± 0.05°, and taken out at the desired interval. The ampoules were chilled, broken open and 1 c.c. of the solution was pipetted out and titrated by the usual iodimetric method.

Decomposition of the Peroxide at 80°.—The decomposition of cinnamoyl peroxide was carried out in a number of solvents at 80°. When the decomposition is brought about by a free radical mechanism, a decrease in the rate of its decomposition in presence of inhibitors is noticed. In our case, experiments in presence of oxygen and hydroquinone showed a marked decreasing effect on the decomposition of the peroxide. Moreover, the peroxide had been successfully used as initiator in the polymerisation of methyl methacrylate (Saha, unpublished work in this laboratory) and styrene (Cooper, *J. Chem. Soc.*, 1951, 3106; 1952, 2408; Saha, *loc. cit.*) and this findings led us to the conclusion that the decomposition of cinnamoyl peroxide was brought about by a free radical mechanism.

TABLE I

Overall decomposition of cinnamoyl peroxide in various solvents at 80°.

Solvent.	Percentage decomposition in 1 hour of (0.02 *M*)		
	Cinnamoyl peroxide.	Benzoyl peroxide.	
		Nozaki *et al.*	Present authors.
Benzene	55.0	15.5	15.5
Toluene	59.6	17 4	17.9
Methylethyl ketone	69.0	...	...
Ethyl acetate	73.3	53.5	53.6
Acetic acid	91.7	59.3	...
Chloroform	50.0	14.5	...
Chlorobenzene	41.7	18.0	...
o-Toluylmethyl ether	40.0	...	...

In Table I the overall % decomposition for cinnamoyl peroxide is recorded along with that for benzoyl peroxide obtained from the work of Nozaki and Bartlett (*loc. cit.*)

and of our own. Work on benzoyl peroxide with benzene, toluene, and ethyl acetate as solvents was carried out as a check of our data. The excellent agreement between our data and those obtained by Nozaki and Bartlett (*loc.cit.*) demonstrates the high degree of reproducibility.

Cinnamoyl peroxide, from Table I, appears to decompose much faster than benzoyl peroxide. The variation of the % decomposition in different solvents shows that the aliphatic solvents tend to have a higher rate than that for aromatic solvents. This is in agreement with Nozaki and Bartlett's work (*loc. cit.*) with benzoyl peroxide. In their case, they have attributed this lower rate of decomposition in aromatic solvents to the inhibiting effect of aromatic products towards the decomposition of benzoyl peroxide.

Determination of Kinetic Constants.—The kinetic order of the reaction was found not to follow that of a unimolecular one, and the rate definitely varied with the concentration. Similar results were also obtained by Bartlett and Altschul (*J. Amer. Chem. Soc.*, 1945, **67**, 816) and Brown (*ibid.*, 1940, **62**, 2657). Hence, it seems likely that decomposition is also a concurrently induced decomposition by the radicals normally present in a solution of decomposing cinnamoyl peroxide, as suggested by Nozaki and Bartlett (*loc. cit*). The kinetic picture according to them may then be represented as:

$$P \xrightarrow{k} 2\,R^{*} \quad \text{(asterisk means free radical)}$$

$$2\,R^{*} \xrightarrow{k_1} R\,R$$

$$R^{*} + P \xrightarrow{k_2} X + R^{*}$$

where P represents peroxide, R^{*}, any free radical and X, the product of chain decomposition. Making the usual approximations

$$R^{*} = \sqrt{kP/k_1}$$

and

$$-\frac{dP}{dt} = k\,P + k_2\,PR^{*}.$$

This may be integrated to furnish

$$\ln\frac{a + \sqrt{P}}{\sqrt{P}} - \ln\frac{a + \sqrt{P_0}}{\sqrt{P_0}} = kt/2$$

where $a = k/k_i = \sqrt{k_1}k/k_2$ and $k_i = k_2\sqrt{k}/k_1$.

This equation after a definite interval of decomposition can be converted into the form for two concentrations of the peroxide.

$$\frac{1}{\sqrt{P_1}} - \frac{C}{\sqrt{P_2}} = \frac{C-1}{a}$$

where C is a constant which is a function of $P_{1.}$ and $P_{2.}$, *i.e.*, the two peroxide concentrations to start with.

From the plot of $1/\sqrt{P_1}$ against $1/\sqrt{P_2}$ 'a' was determined which was utilised towards the plot of $\ln (a + \sqrt{P})/\sqrt{P}$ against 't' to obtain k and k_1. Thus, from our experimental data for overall decomposition rate, we can calculate the true decomposition rate, k, and the relative induced decomposition rate, $k_2/\sqrt{k_1}$. It is not possible to obtain k_2 and k_1 separately.

Rate Measurements at 80°.—The kinetic measurements of cinnamoyl peroxide decomposition in five solvents were carried out and the rate constants were measured (Table II).

TABLE II

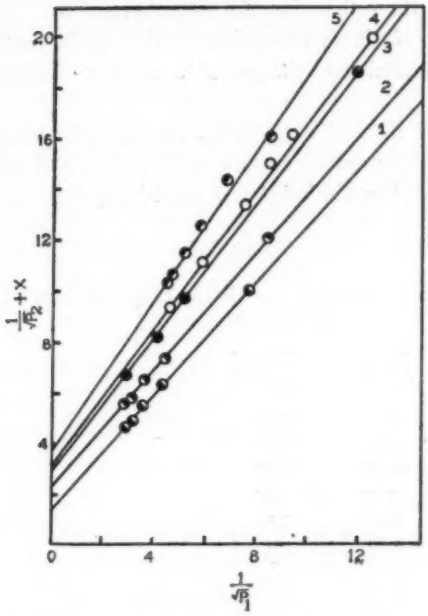
Determination of the rate constants for the decomposition of cinnamoyl peroxide in diff. solvents at 80°.

Solvent.	Time.	$P_1 \times 10^2$ (mols.).	$P_2 \times 10^2$ (mols.).	a.	k (hr^{-1})	k_1 (M/L)$^{\frac{1}{2}}$ (hr^{-1}).	k_1[(M/L)$^{\frac{1}{2}}$ (hr^{-1}).	Benzoyl peroxide * k(hr^{-1}).	Benzoyl peroxide * k_1 (M/L)$^{\frac{1}{2}}$ (hr^{-1}.)
Ethyl acetate	0 min.	4.75	1.90	0.29	1.01	3.45	3.43	0.32	1.32
	15	2.72	1 27		1.08	3.73	3.60		
	30	1.74	0.79						
	45	1.39	0.60						
	60	1.14	0.51						
	90	0.63	0.32						
Methyl-ethyl ketone	0	11.92	4.77	0.36	0.92	2.58	2.70		
	15	8.41	4.49						
	30	5.55	2.68						
	60	3.69	1.72						
	180	0.70	0.70						
Benzene	0	12.05	4.82	0.06	0.16	2.44	6.10	0 12	0.15
	15	9.82	4.46						
	30	7.91	3.38						
	60	5.42	2.55						
	180	1.66	1.02						
Toluene	0	12.60	5.05	0.11	0.25	2.35	4.70	0 12	0.15
	15	9.52	4.72						
	30	7.65	3.39						
	60	5.10	2.55						
	180	1.40	0.83						
o-Toluyl-methyl ether	0	4.75	1.90	0.57	0.67	1.18	1.44		
	15	4.58	1.74		0.69	1.22	1.47		
	30	3.72	1.42						
	60	2.93	1.40						
	120	2.06	0.79						
	180	1.35	0.60						

* Values obtained from the work of Nozaki and Bartlett (*loc. cit.*).

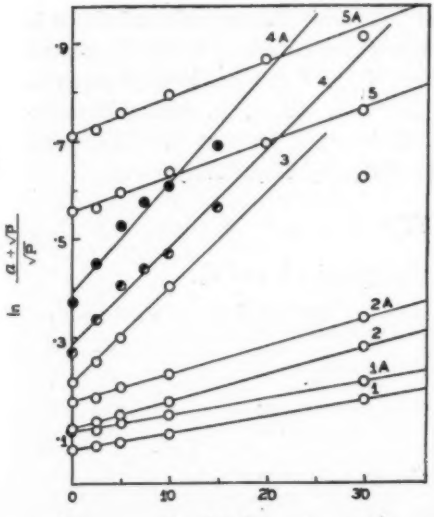
The true decomposition rate, k, in all the solvents is more or less higher with respect to that for benzoyl peroxide. In case of ethyl acetate, it may be observed from Fig. 2 that the slope of the plot of $\ln(a + \sqrt{P})/\sqrt{P}$ vs. 't' has a tendency to fall off with time. This is more marked at 80° than that at 60°, as represented in Figs. 2 and 3. Nozaki and Bartlett (*loc. cit.*) also noticed this trend in the decomposition of benzoyl peroxide in solvents like ethyl acetate, acetic acid and acetic anhydride, and attributed this falling off of the rate of reaction with time to the retarding effect of the aromatic products obtained from the decomposition of the peroxide.

FIG. 1



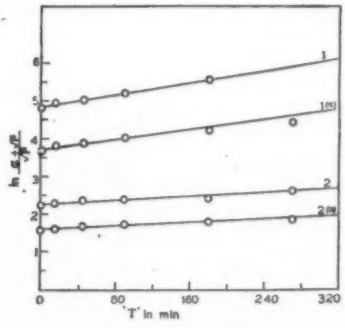
1—Benzene, $x=0$. 2-Toluene, $x=1$ 3—MeEt-ketone, $x=2$.
4—Ethyl acetate, $x=2$. 5—*o*-Toluylmethyl ether $x=3$.

FIG. 2
At 80°.



1, 1A—Benzene. 2, 2A—Toluene.
3—Methylethyl ketone. 4, 4A—Ethyl acetate.
5, 5A—*o*-Toluylmethyl ether.

FIG. 2
At 60°



1, 1A—Ethyl acetate
2, 2A—Toluene.

The value of k_r ($= k_2/\sqrt{k_1}$) in Table II shows that the rate of induced decomposition is much higher than that for the other reaction. The rate k_2 is a type of transfer reaction, whereas k_1 is a termination reaction of the free radicals. This shows that the free radical generated from the peroxide are very efficient in bringing about an induced decomposition.

Rate Measurement at 60°.—To determine the activation energies for the rate constants, experiments were also carried out with ethyl acetate and toluene at a temperature of 60°. The results are listed in Table III and graphically represented in Fig. 3.

TABLE III

Determination of the rate constants for the decomposition of cinnamoyl peroxide in solvents at 60°.

Solvent.	Time.	$P_1 \times 10^2$ (mols.).	$P_2 \times 10^2$ (mols.).	a.	k(hr^{-1}).	k_i(M/L)$^{\frac{1}{2}}$ (hr^{-1}).	k_r(M/L)$^{\frac{1}{2}}$ (hr^{-1}).
Ethyl acetate	0 min.	5.01	2.17	0.30	0.10	0.32	1.03
	15	4.71	1.97		0.12	0.39	1.11
	45	4.41	1.88				
	90	3.97	1.67				
	180	3.34	1.31				
	270	2.86	—				
Toluene	0	5.09	2.20	0.10	0.03	0.32	1 80
	15	4.94	2.13		0.03	0.35	1.87
	45	4.47	1.94				
	90	4.18	1.50				
	180	3.72	1.84				
	270	3.49	1.44				

Applications of the Arrhenius equation gave the activation energies tabulated in Table IV. It is observed that E_k in case of cinnamoyl peroxide is 24 k cals. in toluene and this is lower in comparison with the values of 33.3 k cals. for benzoyl peroxide in benzene by Nozaki and Bartlett (*loc. cit.*) and 29.6 k cals. and 31.0 k. cals. by Kamenskaya and Medvedev (*Acta Physicochim., U. R. S. S.*, 1941, **13**, 565) and McCulure, Robertson and Cuthbertson (*Canadian J. Res.*, 1942, **20B**, 103) respectively.

TABLE IV

Determination of the energy of activation for k and k_1.

Solvent.	Temp.	k(hr^{-1}).	E_k(k cals).	k_i (M/L)hr^{-1}.	E_{ki}(k cals.).
Ethyl acetate	60°	0.11	26.5	0.35	26 7
	80°	1.05		3.59	
Toluene	60°	0 03	23 9	0.33	22.9
	80°	0.25		2.35	

DISCUCSION

The kinetic data and the variation in the rate of overall percentage decomposition with different concentrations of cinnamoyl peroxide in all the solvents studied indicate

definitely that the peroxide undergoes an induced decomposition similar to that for benzoyl peroxide. This is confirmed from our data for this peroxide, which nicely fit the scheme suggested by Nozaki and Bartlett (*loc. cit.*) on the induced decomposition of peroxides.

The higher rate of overall % decomposition for cinnamoyl peroxide (Table I) than that for benzoyl peroxide is contributed by a higher rate of induced decomposition in case of this peroxide. From Table II it may be observed that the value of 'k' in case of cinnamoyl peroxide is higher than that for benzoyl peroxide, and the maximum variation being a three-fold increase in case of ethyl acetate. But that for k_i, the values vary widely. Thus, in benzene and toluene at $80°$, the values of 0.16 and 0.25 respectively for 'k', for cinnamoyl peroxide, may be compared to the value of 0.12 for benzoyl peroxide in both of these solvents. But the value of 2.44 and 2.35, for cinnamoyl peroxide, for k_i in benzene and toluene respectively, is about 15 times higher than the value of 0.15 for benzoyl peroxide in both the solvents. Hence, it can be easily seen that this higher rate for the overall decomposition of this peroxide is contributed predominantly by a high rate of induced decomposition.

This is, however, not unexpected from the structure of the peroxide where an ethylenic double bond is interposed between the phenyl and the carbonyl group in benzoyl peroxide, thus effectively increasing the length of conjugation which is known to have a considerable effect on radical-induced decomposition.

Cooper (*loc. cit.*) in the polymerisation of styrene has also obtained similar results where he has shown that the chain transfer of this peroxide, which is also a radical induced decomposition, is of a fairly high order. He has shown that the value of 1.1 for the chain transfer of the peroxide can be markedly decreased on reduction of the double bond. In his case, the reduction of the double bond gave *bis*-β-phenylpropionyl peroxide, which reduced the transfer value to near about zero, a value roughly the same as that of a normal saturated acyl peroxide. This is also observed from our work with palmitoyl peroxide, the chain transfer of which has been actually found to be near about zero.

One rather unexpected feature, which we like to draw attention to, is the value of the frequency factor for k and k_i. From our data and those from Nozaki and Bartlett (*loc. cit.*), we have calculated the respective frequency factors in case of the two peroxides, which are collected in Table V.

TABLE V

Determination of the frequency factor for k and k_i.

	Present authors.		Nozaki and Bartlett.	
	Cinnamoyl peroxide		Benzoyl peroxide	
Solvent.	Toluene.	Ethyl acetate.	Acetic anhydride,	Benzene.
A_k (sec^{-1})	4.80×10^{10}	2.92×10^{12}	7.85×10^{14}	1.40×10^{16}
A_{ki} (sec^{-1})	9.22×10^{10}	3.62×10^{13}	9.44×10^{11}	1.82×10^{11}

The values (Table V) are of the order of as high as 10^{16} for benzoyl peroxide and 10^{13} for cinnamoyl peroxide. For all unimolecular reactions, the frequency factor generally lies in a region near about 10^{12} and hardly ever exceeds 10^{13}. Our values for cinnamoyl peroxide are within this order, but values of the frequency factor for k, for benzoyl peroxide, are of the order of as high as 10^{16}. This value is rather unexpected but not very unusual, and may be classed with those reactions, for example azide decomposition, where the frequency factor is known to have a value near about this order. It is rather difficult to have a deeper insight into the subject at the present moment and only further experimental work in this line can pronounce the final verdict.

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ION- ACTIVITY MEASUREMENT WITH RESIN MEMBRANE ELECTRODES. BARIUM AND COPPER ION ACTIVITIES IN ELECTROLYTIC SOLUTIONS

By A. S. Basu and S. K. Sinha

Ion-activity of Ba^{2+} and Cu^{2+}, both in very dilute and concentrated solutions, has been satisfactorily measured by the use of resin membrane electrodes, used in other investigation previously by one of the authors (S.K.S.). The membranes were found not to be specific.

Chatterjee and Marshall (*J. Phys. Coll. Chem.*, 1950, **54**, 673) measured the Ba^{2+} ion activity in electrolytic solutions and clays by using clay-membrane electrodes. Similar membrane electrodes were used by Mitra and Chatterjee (*J. Ind. Soc. Soil Sci.*, 1953, **1**, 12) to determine the Cu^{2+} ion activity in solutions of cupric chloride. In case of Ba^{2+} and Cu^{2+} ions, the upper limits of activity measurements were 0.01 and 0.0014 molal respectively.

Joseph (*J. Biol. Chem.*, 1939, **130**, 203) used an electrode of the third kind to measure the Ba^{2+} ion activity in biological system, but the method was somewhat laborious and the measurements were accurate only in fairly concentrated solutions.

In view of the successful use by Sinha (this *Journal*, 1953, **30**, 529) of membrane electrodes prepared from ion-exchange resins for the measurement of the ion activity, an attempt has been made to extend their use to the measurement of Ba^{2+} and Cu^{2+} ion activities.

Experimental

The resin membranes were prepared according to Sinha (*loc. cit.*) from two cation-exchangers, Ionac-C-200 and IRA-100, by moulding at 120°-130° and at 4000/p. s. pressure using polystyrene as a binder. The membranes were fixed to one end of a pyrex tubing with "Durofix" adhesive. They were tested as usual for asymmetry potential and interposed between solutions of known ion activities.

The barium chloride and copper sulphate solutions were so prepared that the ratio of ion activities of successive pairs was 3 : 1, the activity coefficients in very dilute as well as in concentrated solutions being calculated by a graphical extrapolation (Lewis & Randall, "Thermodynamics").

The E. M. F. of the following cell

$$Hg, Hg_2Cl_2 \;|\; \text{Satd. KCl} \;|\; \underset{a_1}{\text{Soln.}} \;\|\; \text{Membrane} \;\|\; \underset{a_2}{\text{Soln.}} \;|\; \text{Satd. KCl} \;|\; Hg_2Cl_2, Hg$$

was measured by means of L & N K_2-type potentiometer in combination with a Hartmann and Braun galvanometer, having a current sensitivity of 10^{-10} amps. mm./m. The E. M. F. readings, accurate within ± 0.1 mv were taken by inter-

changing the solutions inside and outside the pyrex tubing to check as well as eliminate the asymmetry potential, if any. The asymmetry potential, when present, did not exceed 1 mv.

The equilibrium was attained fairly quickly (nearly 15 to 20 minutes) in the concentrated range. Repeated changes of solutions were, however, necessary in the case of dilute solutions. The attainment of equilibrium was also prolonged and more or less constant values were recorded after about 24 hours. Electrically, the membranes performed quite satisfactorily, the resistance not exceeding 0.5 to 0.6 megohms.

The E. M. F.'s recorded in Table I are the mean of duplicate readings not varying beyond 2%. The theoretical E. M. F. s', shown in the last column, have been calculated with the help of the Nernst equation,

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2}.$$

TABLE I

Barium-ion activities in barium chloride solutions and copper-ion activities in copper sulphate solutions.

Activity of cations.		Observed E. M. F. in m v.				Theoretical E.M F. in mv.
a_1.	a_2.	I R A-100.	Mean.	Ionac-C-200.	Mean.	
			Ba-ions.			
0.0729	0.0243	10.8 , 10.5	10.7	11.5, 11.3	11 4	14.1
0.0729	0.0081	21.5 , 21.2	21.4	23.5, 23 4	23.4	28.1
0.0243	0.0081	13.6 , 13.5	13 6	14 5, 15.0	14.7	14.1
0.0081	0.0027	15.0 , 15.1	15.1	14.4, 14.3	14.3	14.1
0.0243	0 0027	29.0 , 29.0	29.0	28.4, 28.6	28.5	28.1
0.0009	0.0003	14.5 , 14.7	14.6	14.2, 14.2	14.2	14.1
0.0003	0.0001	13.3 , 13.2	13.2	13.8, 13 5	13.7	14.1
			Cu-ions.			
0.0081	0.0027	13.8 , 14.5	14.2	15.1, 13.0	14.1	14.1
0.0027	0.0009	14.2 , 14.8	14.5	15.5, 13.0	14.2	14.1
0.0009	0.0003	13.2 , 14.0	14.1	14.5, 14.3	14.4	14.1
0.0003	0.0001	15.0 , 15.0	15.0	14.2, 14.2	14 3	14.1
0.0009	0.0001	28.0 , 29.0	28.5	28.5, 28.6	28.5	28.1

The E. M. F.'s shown in columns 3 and 5 of Table I refer to IRA-100 and Ionac-C-200 respectively. The set of figures to the left corresponds to the arrangements of solutions as shown in columns 1 and 2, whereas the second set to the right has been obtained by interchanging the solutions inside and outside the membrane electrodes. The mean of the two sets is compared with the theoretical E. M. F. shown in the last column.

The resin-membrane electrodes employed in the above experiments therefore quite satisfactorily register the Ba^{2+} and Cu^{2+} ion activities in electrolytic solutions. They measure the activities like the clay-membrane electrodes not only in very dilute solutions (0.0001 for both $[a_{Ba^{2+}} = 0.0243$ and $a_{Cu^{2+}} = 0.0081]$). It would be pointed out here that these membranes like the previous ones are not in any way specific and are therefore able to measure the activities only in absence of other cations.

Thanks are due to Dr. S. K. Mukherjee of the University College of Science for his keen interest and helpful suggestions, and to Dr. P. C. Rakshit, Head of the Department of Chemistry, Presidency College, for his interest and for providing laboratory facilities.

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A NOTE ON THE DERIVATION OF AN EXPRESSION FOR THE EVALUATION OF TRUE ζ POTENTIAL OF PARTICLES FORMING A DIAPHRAGM

By B. N. Ghosh

In a previous paper (this *Journal*, 1955, **32**, 69) the following expression hasbeen derived:

$$\zeta/\zeta_a = 1 + \frac{\alpha}{S}\left(\frac{2p\lambda}{d}\right) \quad \ldots \quad \ldots \quad (1)$$

where ζ_a represents the electrokinetic potential calculated from the Smoluchowski equation, $p\lambda$, the specific surface conductivity and S, the bulk specific conductivity of the solution filling the pores of the diaphragm, and α is a factor greater than unity and equal to $3d/2ra$, as explained later.

It is, however, felt necessary, for avoiding ambiguity, that the assumptions involved in deriving expression (1), the physical significance of α, and the sense of the term 'average radius' represented by d, should be stated clearly.

In a diaphragm consisting of spherical particles of the same radius, r, under a given state of compression characterised by the phase volume ratio, a, it is assumed that the sum of the surface area of all the pores is equal to the sum of the surface area of all the particles, neglecting the sum of the area of the points of contact of the particles. Suppose there are q pores each of average volume, w ml. and of length, l cm. and there are n particles in the diaphragm. Then the surface area of a typical pore is $n.4\pi r^2/q$ which is also equal to $3\pi d^2 l/ra$, as shown in the previous paper (*loc. cit.*), the average radius, d, being defined by the relation $\pi d^2 l = w$. Thus, the volume of the pore of length, l, is put equal to that of a capillary tube of the same length, l, but of cross-sectional area, πd^2. The surface area, $2\pi dl$, of this equivalent capillary tube will be less than that of the pore.

$$\text{Let } \alpha\,(2\pi\, dl) = \frac{3\pi d^2 l}{ra} = \frac{n}{q}.\,4\pi r^2 \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where α is a factor greater than unity.

Then
$$\alpha = \left(\frac{3\pi d^2 l}{ra}\right)\Big/(2\pi dl) = \left(\frac{n}{q}4\pi r^2\right)\Big/(2\pi dl)$$

$$= \frac{3d}{2ra} = \frac{4\pi r^2}{2\pi d\left(\frac{lq}{n}\right)} = \frac{4\pi r^2}{2\pi dl'}$$

where $l' = ql/n$ = the average length of the equivalent capillary tube per particle.

Thus
$$\alpha = \frac{\text{Surface area of a typical pore of length } l.}{\text{Surface area of the equivalent capillary tube of length, } l}$$

$$= \frac{\text{Surface area of a particle}}{\text{Surface area of the equivalent capillary tube of length } l'}.$$

It can be shown, that for a diaphragm consisting of spherical particles of the same radius, at the closest possible packing, $\alpha = 3.3$ approximately.

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CHLOROMETHYLATION OF INDANE

By Sukh Dev

It has been estimated that monochloromethylation of indane produces both the 4-chloromethyl (~ 25%) and the 5-chloromethyl (~ 75%) isomers. The results have been discussed in terms of the steric requirements of the orienting group and the attacking species.

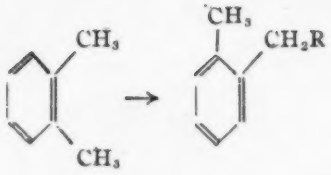
Monochloromethylation of indane has been reported to yield the 5-chloromethylindane exclusively (Arnold, *J. Amer. Chem. Soc.*, 1939, **61**, 1405 ; Arnold and Barnes, *ibid.*, 1944, **66**, 960 ; Plattner and Roniger, *Helv. Chim. Acta*, 1942, **25**, 590). However, the use of this material for synthetic purposes has led to the formation of compounds derived both from the 4- and 5-isomers (Plattner, Heilbronner and Fürst, *Helv. Chim. Acta*, 1947, **30**, 1100). As some of the 5-derivatives of indane were required for our synthetic purposes, it became necessary to find out the extent to which the 4-chloromethylindane was produced in this reaction. The present investigation has revealed that the 4-isomer heavily contaminates the product of monochloromethylation of indane, and as such, this reaction is of doubtful value for the preparation of pure 5-substituted indanes derived from this.

The estimation of the 4-isomer in the product of chloromethylation has been carried out by catalytically reducing this to a mixture of 4- and 5-methylindanes and then finding out the composition of the hydrocarbon mixture by a study of its ultraviolet spectrum and refractive index. The pure 4-methyl- and 5-methylindanes required for this purpose were prepared by the methods outlined below.

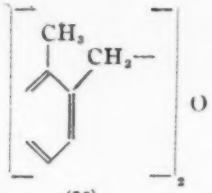
4-Methylindane (IV).—Though the 4-methylindane has been isolated from coal tar (Kruber, *Ber.*, 1924, **57**, 1008), no rational synthesis has been reported. [Losev, Smirnova and Pfeifer (*Z. Obsh. Khim*, 1951, **21**, 668) described a "7-methylindane". A synthesis by Hickinbottom *et al.* (*J. Inst. Pet.*, 1949, **35**, 621) has been mentioned in the *Chem. Abs.*, 1950, **44**, 3433, without any reference to the method of its preparation or properties].

For the preparation of *β-o*-tolylpropionic acid (II), required for the cyclisation to the indanone (III), the present method employing the monobromination of *o*-xylene with N-bromosuccinimide is superior to the method of Mercer and Robertson (*J. Chem. Soc.*, 1936, 288). The structure of the monobrominated product was established as (I) by its conversion to the known *o*-tolylcarbinol (Mettler, *Ber.*, 1906, **39**, 2938). An authentic sample of this alcohol was prepared by the $LiAlH_4$ reduction of ethyl *o*-toluate ; besides the expected *o*-methylbenzyl alcohol, which was obtained in a yield of *ca.* 30%, another crystalline material (m. p. 52-53°) was formed in considerable quantity during this reaction. This has been formulated tentatively as the ether (V).

The Clemmensen reduction of the 4-methylindanone furnished the required 4-methylindane ; a yellow hydrocarbon (m.p. 233-34°) was isolated as a byproduct.



[I, R = Br ;
II, R = $CH_2.CO_2H$]



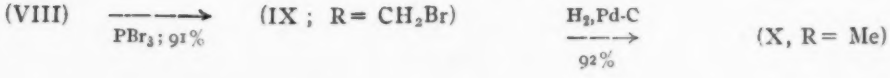
(V)

[III, R = O ; IV, R = H_2]

5-*Methylindane* (X).—It appears that no preparation of pure 5-methylindane has been carried out so far, though the reduction of the so-called "5-chloromethylindane" has been achieved by some workers (Plattner and Roniger, and Arnold and Barnes, *loc. cit.*). The method employed in the present ivestigation is shown below.

(VI)

[VII, R = CO_2H;
VIII, R = CH_2OH;
IX, R = CH_2Br;
X, R = Me]

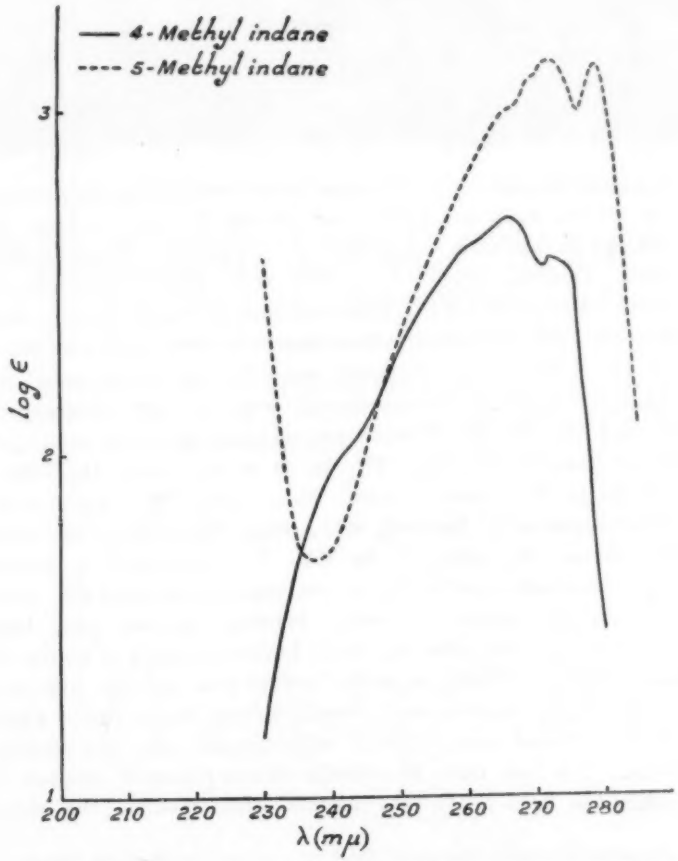


Acetylation of indane is known to attack the 5-position (Braun, Kirchbaum and Schuhmann, *Ber.*, 1920, **53**, 1155; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1940, **62**, 49). (Cf. Borche and Pommer, *Ber.*, 1921, **54**, 102, who presented evidence to show that 4-acetylindane was also produced to a certain extent ; however, acetylindane, prepared by us by the method of Braun *et al.*, yielded derivatives in a pure form and in good yield, proving that essentially pure 5-chloromethylindane was produced under the experimental conditions: see Experimental). The acetylindane could be oxidised to the known crystalline carboxylic acid (VII) by sodium hypobromite. Another efficient consists in procedure the degradation of the methylketone by the Bamberger-Kröhnke reaction (Bamberger, *Ber.*, 1887, **20**, 3344 ; Kröhnke, *ibid.*, 1933, **66**, 604 ; *Z. angew. Chem.*, 1952, **65**, 605) which is carried out *via* the 5-indanacylpyridinium bromide.

The acid was converted into the beautifully crystalline carbinol (VIII) through its ethyl ester by $LiAlH_4$ reduction. The corresponding bromide was readily obtained by the PBr_3 method in an excellent yield. This on catalytic hydrogenation yielded the pure 5-methylindane.

The relation between the composition of binary hydrocarbon mixtures and the refractive index is known to be almost linear (cf. Hawkins and Hunt, *J. Amer. Chem. Soc.*, 1951, **73**, 5379). Knowing n_D^{25} for the pure 4-methyl- and 5-methylindanes and that of the mixture obtainable from the reduction of the monochloromethylated product, the composition of the latter has been computed as ~ 25% of the 4-methyl and ~ 75% of the 5-methyl isomer. The ultraviolet absorption spectra of 4-methyl- and 5-methylindane are shown graphicaliy in Fig. 1.

FIG. 1



The maxima at 272 and 279 mμ were selected for the estimation of the 5-methylindane in the mixture, because at these wave-lengths the absorption due to the other isomer was relatively small (2.56 and 1.64 are the values for log ε of the 4-methylindane

at the wave-lengths 272 mμ and 279 mμ respectively). From the value of ε at these wave-lengths for the hydrocarbon mixture, the proportion of the 5-methylindane was determined to be 75.5%.

Frank and Pierte (*J. Amer. Chem. Soc.*, 1951, **73**, 727) have isolated 4-methyl- and 5-methylindanes from the products of isomerisation of octahydrocoumarins with phosphorus pentoxide. A comparison of the properties recorded by these authors with those now known for the pure compounds indicated that their samples were quite impure.

It is interesting to compare the results of monochloromethylation of indane and some related compounds. The formation of the *o*-isomer is the highest in the case of indane, whereas benzosuberane apparently yields the pure *p*-isomer (Table I).

TABLE I *

No	Compound.	*p*-Isomer. (~%).	*o*-Isomer. (~%).	Reference
1	Benzosuberane	100 **	...	Aspinall and Baker, *J. Chem. Soc.*, 1950, 743.
2	Tetralin	90	10	Vavon *et al*, *Bull. soc chim*, 1939, *v*, **6**, 1025.
3	Indane	75	25	Present work.

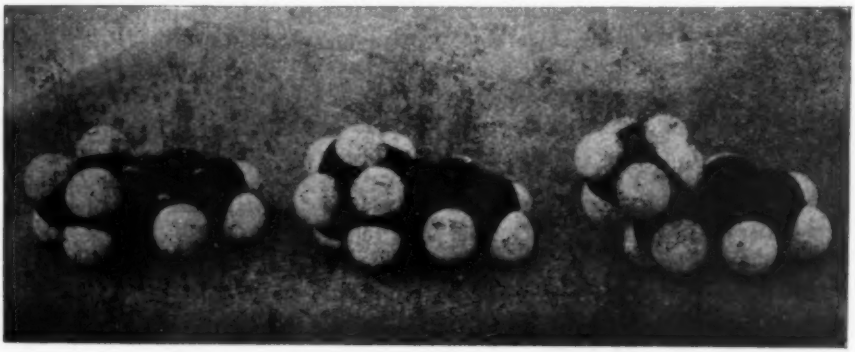
Other factors being the same, the extent of *ortho*-substitution is governed by the steric disposition of the molecule (Nelson and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605; Brown and Bonner, *ibid.*, 1954, **76**, 605; Ferguson, "Electron Structures of Organic Molecules", London, 1952, p. 299). The series indane-tetralin-benzosuberane represents an interesting case where the electrical factors remain almost identical and the statistical factor is ruled out as two "*ortho*" and two "*para*" positions are available. The amount of the *ortho*-isomer produced may then be taken as a measure of the steric hindrance of the methylene group next to the benzene ring. The results indicate that the van der Waal's repulsions decrease in the order: 7-membered > 6-membered > 5-membered ring. This is in accord with the order obtained by Arnold and Craig (*J. Amer. Chem. Soc.*, 1950, **72**, 2728) from various physical and chemical studies (cf. Kadesch, *ibid.*, 1944, **66**, 1208. This author shows from chemical evidence the order to be CH_3 > 7-membered > 5-membered > 6-membered ring). Molecular models (Fig. 2) also appear to support this order. If we assume that the distance (centre to centre) between the two axial hydrogens in *cyclo*hexane can represent the effective steric hindrance range in similar compounds, then the distance between the hydrogen on the benzene ring and the hydrogens on the α-methylene group of the alicyclic series should decrease in the order: 5-membered > 6-membered > 7-membered ring. Actual measurements on the models (Catalin Molecular Models. The fact that a five-membered ring cannot be properly constructed from these models has been taken into account while making the measurements.

* In order to obtain more accurate comparable data, it is necessary that the various hydrocarbons should be chloromethylated under identical conditions; such a study is in progress.

** This value was based on the fact that the chloromethylated product yielded on conversion the corresponding acetic acid in a pure form.

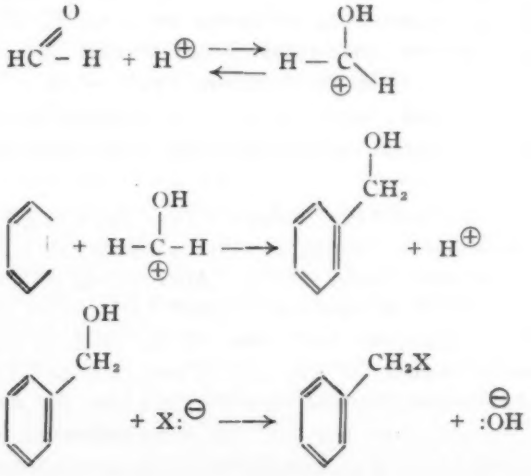
Alicyclic ring of tetralin was built as a deformed chair; in benzosuberane the chain of five methylene groups was constructed from the energetically more favourable constellations possible) gave the values as 32 mm., 26 mm. and 21 mm., the distance between the two axial hydrogens of *cyclo*hexane ring being 25 mm.

FIG. 2



Indane. Tetralin. Benzosuberane.

Another steric factor which will govern the extent of *ortho* substitution is the bulk of the attacking group (vide Ingold, "Structure and Mechanism in Organic Chemistry", New York, 1953, p. 259). Halomethylation, possibly, proceeds by an electrophilic attack of the aromatic nucleus by a hydroxymethylene cation ($HOH_2C^{\oplus}$) followed by a displacement reaction involving the anion $\ddot{X}:^{\ominus}$ (cf. Bartlett in Gilman's "Organic Chemistry, An Advanced Treatise", Vol. III, p. 113). Acetylation of indane produces more or less pure 5-acetylindane.



Since the reactivity of the acetylium ion (it is generally agreed that the Friedel-Crafts acylation proceeds by the attack of acylium ion, RCO^+, e. g. vide Beddley and Voss, *J. Chem. Soc.*, 1954, 418) is comparable to that of chloromethylating species (Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292) and since its steric requirements cannot be very different from those of $\oplus CH_2OH$, it is difficult to see why in the acetylation of indane the 5-isomer is produced practically exclusively. A possible explanation can be that some other bulkier complex intermediate is involved in such acylations. A similar view-point has been expressed recently by other authors (Tedder, *Chem. Ind.*, 1954, 630; Brown and Bonner, *loc. cit.*, also Ingold, *loc. cit.*, p. 297).

EXPERIMENTAL

Anhydrous sodium sulphate was used for drying the extracts. All melting and boiling points are uncorrected. Petroleum ether refers to the fraction, b.p. 40°-60°.

o-Methylbenzyl Bromide (I) (cf. Misra and Shukla, this *Journal*, 1951, **28**, 277).—A mixture of dry *o*-xylene (53 g., 0.5 *M*) and CCl_4 (200 c.c.) containing a little benzoyl peroxide (0.5 g.) was placed in a flask (1 litre) and one-third of 0.5 moles (89. g., coarsely powdered) of purified N-bromosuccinimide (NBS) was added and the whole cautiously heated to refluxing (anhydrous conditions); the vigour of the reaction was controlled, when necessary, by cooling the reaction mixture in ice-water for a short while. The remaining two additions of NBS were made at intervals of half-an-hour and the reaction carried out as before. With each addition of NBS, 0.5 g. of benzoyl peroxide was also introduced. Finally (after 1½ hours) an additional lot of benzoyl peroxide (0.5 g.) was added and the mixture refluxed for another 3 hours. After cooling in an ice-bath, the succinimide (50 g., 100%) was filtered off and washed with CCl_4 (25 c.c. × 2). The combined filtrate and washings were first washed with ice-cold $NaHCO_3$ solution (5%, 50 c.c. × 2) and finally with brine (50 c.c.). From the dried solution, the solvent was removed and the residue fractionated (Vigreux column; 10") under vacuum: (*i*) 1st fraction, b.p. 50°-55°/30 mm., 6.0 g. (11.3%), identified as *o*-xylene; (*ii*) 2nd fraction represented *o*-methylbenzyl bromide and had b.p. 102°/15 mm., n_D^{27}, 1.5730, highly lachrymatory, yield 63.0 g. (68.1%); (*iii*) 3rd fraction (b.p. 128-30°/4.5 mm., yield 13.2 g., 10%) solidified to a solid, m.p. 90-93°, identical with *o*-xylyl dibromide, prepared according to the method of Perkin (*J. Chem. Soc.*, 1888, **53**, 5).

o-Toiylcarbinol: (*i*) *From Ethyl Toluate*.—To a slurry of $LiAlH_4$ (3.8 g., 0.1 *M*) in ether (50 c.c.) was added a solution of ethyl *o*-toluate (26 g., 0.158*M*) in ether (50 c.c.) during ½ hour, with vigorus stirring. After stirring at room temperature (23°) for another ½ hour the reaction mixture was refluxed for 2 hours and then left aside for 24 hours. After working up with dilute H_2SO_4 (10%) in the usual manner, the product was fractionated to yield (*a*) b.p. 135°/50 mm., 6.0 g. (31.5%), recrystallised from a mixture of petroleum ether and ether at 0° in white, flat needles, m.p. 37-39°, yield 5 g. (Mettler, *loc. cit.*, gives m.p. 35° for *o*-tolylcarbinol); (*b*) b.p. 216-17°/50 mm., 9.5 g., recrystallisation at 0° from dilute acetone gave prismatic needles (8.0 g.),

m.p. 52-3° (Found: C, 84.4, 84.9; H, 8.5, 8.0. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0 per cent).

(*ii*) *From o-Xylyl Monobromide.*—A mixture of *o*-methylbenzyl bromide (4.6 g., 0.025 *M*) and fused sodium acetate (12.3 g., 0.15*M*) in glacial acetic acid (25 c.c.) was gently refluxed (9 hrs.). After dilution with water the pleasant smelling acetate was isolated by ether extraction. This was refluxed with absolute ethyl alcohol (100 c.c.) containing sulphosalicylic acid (25 mg.) for 5 hours. Most of the alcohol was slowly fractionated off and the cooled residue diluted with water (100 c.c.). The carbinol was taken up in ether (20 c.c. × 3) and the solution after washing with brine (15 c.c. × 3) was dried. Removal of the solvent, followed by distillation, furnished *o*-tolyl carbinol, b.p. 134-38°/50 mm., yield 2.0 g., m.p. 37.9° (mixed m.p. with the above sample remained undepressed).

β-o-Tolylpropionic Acid (II).—The sodium salt of malonic ester was prepared from molecular sodium (5.75 g., 0.25 g. atoms) and the ester (56.0 g., 0.35*M*) in dry toluene (200 c.c.). This was cooled in an ice-bath and treated with *o*-methylbenzyl bromide (46.3 g., 0.25 *M*) in one lot; 20 c.c. of toluene was used for washing in the last traces. After keeping at room temperature for ½ hour, the reaction mixture was heated (2 hrs.) on the steam-bath with occasional swirling; it was finally refluxed for another 12 hours. The cooled reaction mixture was poured on to water, the toluene layer separated, washed with dilute acetic acid (2%, 150 c.c.) and finally with saturated ammonium sulphate solution (150 c.c. × 2). After drying, the solvent was removed (column) and the residue fractionated to furnish ethyl *o*-xylylmalonate as a colorless, mobile liquid, b.p. 130°/1 mm., n^{28}, 1.4905; yield 60.0 g. (91%). (Found: C, 68.8; H, 7.8. $C_{13}H_{20}O_4$ requires C, 68.2; H, 7.6 per cent).

The above ester (52.8 g., 0.2 *M*) was refluxed with HCl (150 c.c.) in acetic acid (100 c.c.) containing water (25 c.c.) for 18 hours. The product was cooled, diluted with ice-water and the separated acid collected after an hour; it was washed with water and dried; yield of the crude acid was quantitative, m.p. 99-100°. Recrystallisation from a mixture of acetic acid (100 c.c.) and water (150 c.c.) gave white flat needles and plates, m.p. 104°, yield 31.0 g. (95%). Mercer and Robertson (*loc. cit.*) report m.p. 104-105° (cf. Plattner and Wyss, *Helv. Chim. Acta*, 1940, **23**, 907).

4-Methylindanone (III).—To polyphosphoric acid (P_2O_5, 150 g. and 89% orthophosphoric acid, 90 c.c.) was added the above acid (15.0 g.) in one lot. The mixture was carefully swirled (silica-gel guard tube) over a free flame till the acid melted to a clear brown solution. This was finally heated on the steam-bath for 2 hours with occasional agitation. The deep coloured product was poured on to ice (400 g.) and water (400 c.c.), stirred and left overnight. The ketone was collected by filtration, m.p. 80-85°, yield 14.0 g. This was purified by distillation, b.p. 144°/13 mm., m.p. 99-100°, yield 10.5 g. (71.2%). Recrystallisation from a mixture of benzene and pertoleum ether gave white prismatic needles, m.p. 99-100° (constant). Mercer and Robertson (*loc. cit.*) give m.p. 103-104°.

The 2:4-*dinitrophenylhydrazone* was prepared by the HCl method. Recrystallisation from a large volume of pyridine gave fine, orange-red needles, m.p. 294° (decomp.),

when introduced in a bath at 285°. (Found: N, 17.3. $C_{16}H_{14}O_4N_4$ requires N, 17.2 per cent).

4-Methylindane (IV).—Amalgamated zinc wool (zinc wool, 22 g. and mercuric chloride, 2.2 g.) was covered with water (30 c.c.), HCl (70 c.c.) and toluene (30 c.c.) and the above indanone (7.3 g.) along with glacial acetic acid (2 c.c.) was introduced. The mixture was refluxed for 32 hours and a total of 100 c.c. of HCl was added in suitable instalments. The toluene layer was deep yellow and some crystals could be seen floating in this layer (cooled). After adding ether (50 c.c.), the solvent layer was separated, washed with water and finally with brine (50 c.c. × 2) and dried. Removal of the solvent afforded a yellow residue, which was diluted with petroleum ether (15 c.c.), and after cooling, the solid (product A) was collected and washed with petroleum ether (5 c.c. × 2). The yellow petroleum ether solution was filtered through a column of alumina (Basic/I; 150 mm. × 12 mm.), which was washed with petroleum ether (35 c.c.); the column retained a yellow band (80 mm.), which could be eluted with ether (not investigated further). The colorless eluterate on rectification furnished the desired indane, b.p. 107-108°/40 mm., yield 5.0 g. (75.7%). This was further fractionated over sodium and the central cut (3.0 g.) selected for physicochemical measurements; b.p. 107.5°/40 mm., 112°/50 mm., n_D^{25}, 1.5336; n_D^{20}, 1.5316; d_4^{20}, 0.9467; M_D, 43.07 (calc. 42.58; EM_D, 0.49; $E\Sigma_D$, 0.40). (Found: C, 90.6; H, 9.1. $C_{10}H_{12}$ requires C, 90 9; H, 9.1 per cent).

The yellow plates (product A) had m.p. 233-34°, but the yellow powder obtained by sublimation at 160°/1 mm. melted at 230°; both the samples gave identical data. (Found: C, 92.7, 92.3; H, 7.5, 7.8. $C_{20}H_{20}$ requires C, 92.3; H, 7.7 per cent).

5-Acetylindane (VI).—A mixture of indane (59.0 g., 0.5 *M*; Sukh Dev, this *Journal*, 1953, **30**, 729), acetyl chloride (42 g.) and CS_2 (250 c.c.) was well chilled in an ice-salt bath and treated with stirring and cooling with aluminium chloride (72 g., coarse), the addition of the latter being made in three equal lots during 25 minutes; a bright orange complex separated. After stirring for 1 hour at 0-5° and 2 hours at room temperature, the mixture was worked up as usual. Yield of the acetylindane (b. p. 144°/13 mm.) was 70 g. (87.5%).

The 2:4-*dinitrophenylhydrazone* was prepared by the hydrochloric acid procedure in quantitative yield and the crude material had m. p. 265-66°. It crystallised as deep-red micro-prisms from a large excess of pyridine, m. p. 266-67° (decomp., constant). (Found: N, 16.2. $C_{17}H_{16}O_4N_4$ requires N, 16.4 per cent).

Indane-5-carboxylic Acid (VII): *(i) By Sodium Hypobromite Oxidation* (cf. Borsche and Pommer, *loc. cit.*).—A solution of sodium hypobromite was prepared from bromine (120 g., 0.75 *M*) and sodium hydroxide (82.5 g., 2.06 *M*) in water (700 c. c.). To this the above ketone (40 g., 0.25 *M*), dissolved in purified dioxane (100 c. c.), was added (0°) with stirring during 5 minutes. The temperature was raised to 40° during ½ hour and the mixture stirred at 45° ±5° for 1 hour and then at 75°-82° for 45 minutes. After cooling and dilution with water (100 c. c.), it was extracted with CCl_4 (75 c. c. × 2) and the alkaline solution on acidification with concentrated hydrochloric acid furnished the crude acid, which was redissolved in dilute Na_2CO_3 solution and after clarification with norite, followed by acidification (p_H 2), yielded a cream-coloured product, m. p.

175-81°, yield 30 g. Recrystallisation from acetic acid (300 c. c.) plus water (50 c. c.) furnished white, flat needles, m. p. 183-84°, yield 27 g. (66.6%).

*(ii) By Bamberger-Kröhnke Degradation**.—5-Acetylindane (24 g., 0.15 *M*) in dry ether (100 c. c.) along with anhydrous aluminium chloride (0.1 g.) was well chilled in ice-salt bath and with stirring (Mag-mix.) dry bromine (24.8 g., 0.31 g. atom) was introduced dropwise. After the addition of first one to two grams of bromine, one has to wait (10-15 mins.) till it is decolorised and it may also be necessary to remove the ice-bath momentarily to initiate the reaction. The absorption of the remaining bromine was rapid (5 mins.). The solvent was then immediately removed by suction in a thin stream of dry air, when the ω-bromo compound was left as a pale crystalline residue. This was taken up in absolute alcohol (75 c.c.) immediately and anhydrous pyridine (14.6 g.) was added to the suspension at room temperature with stirring during 5 minutes. The stirring of the clear, almost colorless solution was continued when the mixture warmed up and a white solid started precipitating out. After stirring for a total of 25 minutes at room temperature, the reaction mixture was refluxed for 15 minutes to complete the formation of the 5-indanacylpyridinium bromide.

The acid-fission of the above salt was carried out by adding the suspension, with stirring, to a cold solution of sodium hydroxide (15 g. in 300 c. c. of water); the addition was made in several lots during 7 minutes and a total of 80 c. c. of ethanol was used for transferring in the adhering pyridinium bromide. Each addition produced a deep orange-red colour, which was quickly discharged with the precipitation of a little black tarry material. Finally it was heated on a water-bath for 30 minutes, water (300 c. c.) added, treated with active charcoal (3 g.) and filtered. The almost colorless filtrate on acidification yielded the desired acid, m. p. 177-81°, yield 19 g. This was recrystallised as above to furnish the pure acid (17 g., 70%), m. p. 183-84°. The m.p. given in the literature (Elsevier, "Encyclopaedia of Organic Chemistry", **12A**, p. 358) for the indane-5-carboxylic acid is 183°; the 4-isomer melts at 153·5°.

The S-*benzylthiuronium* salt crystallised from alcohol in white silky needles, m. p. 174-74.5° (with efferv.). (Found: N, 8.5. $C_{18}H_{20}O_2N_2S$ requires N, 8.5 per cent).

The p-*phenylphenacyl ester* was prepared in the usual manner and was obtained from aqueous dioxane as white, microscopic plates, m.p. 140-41°. (Found: C, 80.5; H, 5.8. $C_{24}H_{20}O_3$ requires C, 80.9; H, 5.6 per cent).

Ethyl Indane-5-carboxylate.—A mixture of the above acid (38 g.), benzene (60 c. c.), ethanol (35 c. c.) and concentrated sulphuric acid (5 c. c.) was refluxed for 28 hours. Working up in the usual manner furnished the ester as a colorless liquid, b.p. 156°/20 mm., yield 41 g. (92%). An analytical sample had n_D^{24}, 1.5330; d_4^{24}, 1.070; M_D, 55.38 (calc. 53.48; EM_D, 1.90; $E\Sigma_D$, 1.00).

5-Indanylcarbinol (VIII).—The above ester (38 g., 0.2 *M*) in ether (70 c. c.) was reduced with a slurry of lithium aluminium hydride (9·4 g., 0.13 *M*) in ether (100 c. c.), as described above for *o*-tolylcarbinol. Some solid alcohol separated out on decomposition of the reaction mixture with dilute sulphuric acid (10%) in the usual manner; hence

* Arnold, Murai and Dodson (*J. Amer. Chem. Soc.*, 1950, **72**, 4193) degraded this ketone via 5-indanacylpyridinium iodide in poor overall yields.

sufficient benzene (50 c. c.) was added to dissolve the solids, and the ether-benzene layer after having been washed with 1% Na_2CO_3 solution in brine (100 c c.) was dried. The product was stripped off the solvent and the crystalline residue was recrystallised from dilute acetone (first at 0° and then at −10°) to yield27.0 g. (91.2%) of a product, m.p. 70-72°; the mother-liquor on working up afforded another 1.5 g. of a slightly less pure material (m. p. 68-70°). An analytical sample was prepared by two recrystallisations from a mixture of benzene and petroleum ether in white, silky needles, m.p. 73.5-74.5°. (Found : C, 81.4 ; H, 8.0. $C_{10}H_{12}O$ requires C, 81.1 ; H, 8.1 per cent).

5-Bromomethylindane (IX).—The above alcohol (27 g., 0.182 *M*) was dissolved in a mixture of benzene (20 c. c.) and chloroform (50 c. c.). Two drops of anhydrous pyridine were added and after chilling in an ice-salt bath, phosphorus tribromide (16.8 g., 0.062 *M*) was introduced during 5 minutes. The reaction mixture was kept in the Frigidaire for 20 hours, then at room temperature (25°) for 2 hours and finally at 60°-70° for another six hours. After cooling and diluting with ice-water, the solvent layer was separated after adding some ether ; this was washed wirh water (ice-cold ; 75 c.c.), brine (75 c.c.) and then dried. The solvent was removed and the residue fractionated to furnish the bromide as a colorless, lachrymatory liquid, b. p. 116-17°/4 mm., n_D^{30}, 1 5900; yield 34.0 g. (91%). An analytical sample had b. p. 128°/7 mm., n_D^{30}, 1.5900 ; d_4^{30}, 1.376 ; M_D, 51.74 (calc. 50.34 ; EM_D, 1.4 ; $E\Sigma_D$, 0.66). (Found : Br, 37.5. $C_{10}H_{11}Br$ requires Br, 37.9 per cent).

5-Methylindane (X).—The above bromide (4.2 g.) in ethyl alcohol (50 c. c.) was shaken in an atmosphere of hydrogen in the presence of 5% Pd-C (0.5 g.). Reduction came to a close (40 mins.) after the absorption of the theoretical volume of hydrogen. The catalyst was filtered off and washed with petroleum ether (15 c c. × 3). Water (75c.c.) was added to the filtrate and the petroleum ether layer separated. This was washed with brine (20 c. c. × 2) and dried (activated silica gel). Rectification gave the desired hydrocarbon, b. p. 103°/40 mm., yield 2.4 g. (92.3%). An analytical sample (central cut) was obtained by refractionation over sodium, b. p. 110°/ 50 mm., n_D^{28}, 1.5300 ; n_D^{30}, 1.5280 ; d_4^{30}, 0.9386 ; M_D, 43.22 (calc. 42.58; EM_D, 0.64; $E\Sigma_D$,0.52). (Found : C, 90.8 ; H, 9.1. $C_{10}H_{12}$ requires C, 90.9 ; H, 9.1 per cent).

Chloromethylation of Indane.—A mixture of indane (59.0 g., 0.5 *M*), paraformaldehyde (28 g.), glacial acetic acid (64 c. c.), syrupy phosphoric acid (*d* 1. 85, 41 c. c.) and hydrochloric acid (100 c. c.) was vigorously stirred at 60° ± 3° for 16 hours. The product was cooled, diluted with ice-cold water (250 c. c.) and extracted with ether (75 c. c. × 2). The extract was washed with cold water (100 c. c.), brine (100 c. c.) and then dried. After removal of the solvent the product was fractionated to furnish chloromethylindane, b. p. 118°/8 mm., yield 45.0 g. (54.2%); 20 g. (33.8%) of indane was recovered as a fore-run. This was refractionated to furnish a material having b.p. 107°/4 mm., n_D^{21}, 1.5625 ; d_4^{21}, 1.116 ; M_D, 48.39 (calc. 47.44 ; $E\Sigma_D$, 0.57) (cf. Arnold, *loc. cit.*).

Reduction of Chloromethylindane.—The above chloromethylindane (9 g.) in ethyl alcohol (60 c. c.) was catalytically reduced (6 hrs.) over palladium-carbon (5%, 0.5 g.) to furnish a quantitative yield of the methylindane, b.p. 103-106°/40 mm. (for details see

5-methylindane). This was redistilled over sodium for physicochemical measurements, b. p. 110-12°/50 mm., n_D^{25}, 1.5309.

Estimation of Isomers.—(*i*) Since the n_D^{25} for the mixture is 1.5309 and the corresponding values for the 4-methyl and 5-methyl isomers are 1.5336 and 1.5300 respectively, the amount of 4-isomer in the mixture has been calculated to be 25%.

(*ii*) The ultraviolet spectra were measured on a Beckmann DU spectrophotometer using 95% ethanol as the solvent; the readings were taken at intervals of 2 mμ, at turning points at intervals of 1 mμ; light absorption for 4-methylindane: λ_{max_1} 266 mμ, log ϵ_1 2.68; λ_{max_2} 273, log ϵ_2 2.606; for 5-methylindane: λ_{max_1} 272, log ϵ_1 3.14; λ_{max_2} 279, log ϵ_2 3.127. The values of log ϵ for the hydrocarbon mixture at 272 mμ and 279 mμ were 3.0622 and 3.0068 respectively. The estimation was carried out in the usual manner (e.g., vide Tunnicliff *et al.*, *Anal. Chem.*, 1949, **21**, 890; Vaughn and Stearn, *ibid.*, p. 1361).

Molecular Refractivities of Indane Derivatives.—Data presented in the present communication indicate that derivatives of indane show a definite exaltation. This is also borne out by the values recorded by other authors (Plattner and Roniger, *loc. cit.*, Frank and Pierle, *loc. cit.*).

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α-PICOLINE COMPLEXES OF ZINC, CADMIUM, COBALT AND NICKEL THIOCYANATES

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α-Picoline complex of thiocyanates of zinc, cadmium, cobalt and nickel have been prepared and their properties and compositions determined. The stability of these complexes has been determined both by dissociation pressure measurements and thermochemical methods. The values obtained by the two methods agree closely It has been found that the stability of the complex, which contains the lowest number of α-picoline molecules, is not always the greatest. The influence of the anion of the salt forming the complex has been discussed.

In the present investigation α-picoline complexes of the thiocyanates of Zn, Cd, Co and Ni have been prepared and their stabilities determined by dissociation pressure experiments and direct thermochemical measurement with a view to ascertaining the influence of the anion on the stability of the complex, as there is no record in literature regarding the α-picoline complexes of the same.

Experimental

The thiocyanates of the above metals were prepared in the laboratory starting from the preparation of barium thiocyanate by the method described by Newton Friend ("Text-book of Inorganic Chemistry", Vol. III, Part I, p. 257). Zinc thiocyanate was obtained from barium thiocyanate by following the method of Wells (*Amer. Chem. J.* 1902, **28**, 245), cadmium thiocyanate by that of Grossmann (*Ber.*, 1902, **35**, 2666), cobalt thiocyanate according to that of Grossmann and Hünseler (*Z. anorg. Chem.*, 1905, **46**, 368) and nickel thiocyanate in the manner described by Grossmann (*Ber.*, 1904, **37**, 565). The purity of the compounds were established by analysis. They had the formulae : $Ba(CNS)_2.2H_2O$, $Zn(CNS)_2.2H_2O$ [the zinc thiocyanate lost water of crystallisation at 30°, being converted into $Zn(CNS)_2$]. $Co(CNS)_2.4H_2O$ (cobalt thiocyanate was unstable in air and had to be preserved out of contact with air) and $Ni(CNS)_2$ (which contained no water of crystallisation).

Freshly prepared thiocyanates of these metals were found to be soluble in α-picoline. The crystalline thiocyanate (2-4 g.) was dissolved in freshly distilled α-picoline, the solution being completed by heating on a water-bath. There should be a slight excess of thiocyanate crystals in the liquid. The solution was filtered hot quickly through a small Büchner funnel. The residue consisting mainly of undissolved thiocyanate remained on the filter and the clear filtrate, on cooling to the room temperature, yielded beautiful shining crystals of the complex. The crystals were filtered, made free of α-picoline by suction, and dried by pressing between folds of filter papers.

The crystalline complexes of Zn and Cd are colorless. They are not hygroscopic, perfectly stable in air and completely soluble in water. Zn complex is highly soluble in chloroform and acetone ; the cadmium complex is insoluble in chloroform and only

partially soluble in acetone. Both are insoluble in benzene and ether. The colour of the cobalt complex is rose-red and that of nickel, pale blue. They are stable in air at the ordinary temperatures and are sparingly soluble in water. They are moderately soluble in alcohol, the cobalt compounds forming a blue solution. Both of them are highly soluble in acetone and sparingly soluble in benzene. They are both insoluble in ether.

The composition of the complexes has been established by analysis. The estimations of α-picoline, Zn, Cd, Co and Ni were carried out in a similar manner as described in a previous paper (this *Journal*, 1955, **32**, 317). The thiocyanate was estimated by dissolving a weighed quantity of the complex in water, acidifying with a few drops of nitric acid and precipitating as silver thiocyanate. The precipitate was filtered in a sintered glass crucible, washed with water and a little alcohol and dried at 130°. The results of analysis are recorded in Table I.

TABLE I

	$Zn(CNS)_2$. 2 pico.		$Cd(CNS)_2$ 4pico.		$Co(CNS)_2$. 4 pico.		$Ni(CNS)_2$. 4 pico.	
	*Found.	Calc.	*Found.	Calc.	*Found.	Calc.	*Found.	Calc.
M	17.5%	17.7%	18 7%	18.7%	11.1%	10.9%	10.7%	10.7%
CNS	31.5	31.5	19.5	19.3	21.5	21.2	20 9	21.2
Pico	50.8	50.6	62.2	61.9	68.3	68.0	69.5	68 0

*Mean of three estimations

It will be seen that none of these complexes contain water and therefore heats of dissociation can be determined easily. The dissociation pressures of the complexes were measured at different temperatures using the same apparatus as described by Ray and Sinha (*Trans. Faraday Soc.*, 1948, **44**, 790) and from these data the heat of dissociation, which gave a measure of the stability of the complex, was calculated. An electrically operated air thermostat, kept constant to ± 0.1°, was used. The thermostat was set at different temperatures and when equilibrium was attained the pressure obtained from the difference in the heights of mercury in the manomoter was read by means of a cathetometer. It is necessary to know the vapour pressure of α-picoline at different temperatures for finding out whether the dissociation pressure measured is that of the complex or of free α-picoline. As no data for these can be found in literature, the vapour pressures of α-picoline were first determined, using the same apparatus. The vapour pressures of α-picoline at different temperatures are shown in Table II, and the values obtained for the dissociation pressures of the complexes are recorded in Tables III-VIII.

TABLE II

α-Picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.
39.4°	30.6 mm.	3200	1 4857	60.0°	78.1 mm.	3003	1.8927
45.1°	39.0	3145	1.5910	65.0°	95.0	2959	1.9777
50.3°	51.0	3093	1.7076	69.5°	115.6	2920	2 0639
54.4°	61.0	3055	1.7853	75.0°	141.3	2874	2.1501

TABLE III

System $Zn(CNS)_2$. 2/1 α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.
50.0°	4.2 mm.	3096	0.6232	74.0°	10.0 mm.	2882	1.0000
55.0°	5.1	3049	0.7076	81.5°	13.0	2821	1.1139
61.0°	6.4	2994	0.8062	87.2°	15.9	2776	1.2014
65.0°	7.3	2952	0.8633	91.0°	17.6	2748	1.2455
67.5°	8.0	2937	0.9031				

Mean value of the heat of dissociation (calculated from the graph) is 8,244 calories.

TABLE IV

System $Cd(CNS)_2$. 4/3-α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.
40.0°	5.9 mm.	3196	0.7700	65.0°	20.0 mm.	2959	1.3010
45.0°	7.6	3145	0.8800	71.8°	27.5	2900	1.4390
49.7°	9.9	3099	0.9950	76.5°	33.1	2862	1.5190
54.5°	12.4	3054	1.0930	85.2°	48.4	2792	1.6850
60.0°	15.9	3003	1.2010	90.0°	58.8	2755	1.7700

Mean value of the heat of dissociation (calculated from the graph) is 10, 341 calories.

TABLE V

System $Cd(CNS)_2$.3/2-α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.
55.0°	7.1 mm	3049	0.8510	75.0°	21.4 mm.	2874	1.3300
60.0°	9.8	3003	0.9910	80.7°	28.2	2827	1.4500
65.0°	12.5	2959	1.0970	85.5°	36.3	2789	1.5590
70.0°	16.6	2916	1.2200	90.0°	45.6	2755	1.6590

Mean value of heat of dissociation (calculated from the graph) is 12,534 calories.

TABLE VI

System $Cd(CNS)_2$. 2/0-α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10} p$.
65.0°	6.0 mm.	2959	0.7780	85.0°	11.0 mm.	2794	1.0410
70.0°	7.1	2916	0.8510	90.0°	12.6	2755	1.1000
75.0°	8.1	2874	0.9080	95.0°	14.5	2717	1.1610
80.0°	9.8	2832	0.9910				

Mean value of the heat of dissociation per molecule of picoline (as calc. from the graph)is 7,242 calories.

TABLE VII

System $Co(CNS)_2$. 4/3-α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.
65.0°	4.5 mm.	2959	0 6532	85.0°	13.5 mm.	2794	1.1303
70.5°	6.0	2912	0.7824	88.5°	16.5	2767	1.2175
75.2°	8 2	2872	0 9138	95.0°	22.4	2717	1.3500
79.6°	10.3	2835	1.0128				

Mean value of the heat of dissociation (as calculated from the graph) is 13,245 calories.

TABLE VIII

System $Ni(CNS)_2$. 4/3-α-picoline.

Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.	Temp.	Pressure.	$1/T \times 10^6$.	$\log_{10}p$.
65 0°	6.3 mm.	2959	0.8010	85 9°	16.8 mm.	2786	1.2279
70.3°	8.1	2913	0.9085	91.7°	20.8	2744	1.3181
74.5°	10.0	2878	1.0000	95.0°	24.0	2717	1.3800
80.2°	12.9	2831	1.1107				

The mean value of the heat of dissociation (as calculated from the graph) is 11,005 calories.

The latent heat of vaporisation in the case of α-picoline and the heat of dissociation of the complexes can be calculated from the pressure-temperature data by means of the Clapeyron-Clausius equation,

$$d \ln p/dt = Q/RT^2$$

which on integration gives

$$\ln p = -\frac{Q}{RT} + \text{const. or } \log_{10}p = -\frac{Q}{4.576} \cdot \frac{1}{T} + \text{const.},$$

where Q is the heat of vaporisation or the heat of dissociation and p is the dissociation pressure at the absolute temperatures, T. To calculate the value of Q, it is therefore necessary to plot the logarithms of p against reciprocals of T. For convenience, the values of $\log_{10}p$ have been plotted against the corresponding values of $1/T \times 10^6$ and straight line graphs obtained.

The pressure-composition isothermals of the complexes of α-picoline with the thiocyanates of Zn, Cd, Co and Ni have been determined. The apparatus and the method used have been described in a previous paper by Sinha and Bhattacharya (*loc. cit.*). The results obtained are represented graphically in Figs. 1-4.

From Figs. 1-4 it appears that $Zn(CNS)_2$. 2 pico exists in one solid phase at 65°, three solid phases, $Cd(CNS)_2$. 1 pico, $Cd(CNS)_2$. 3 pico and $Cd(CNS)_2$. 2pico in the case of cadmium complex at the same temperature, and only one stable solid phase each, namely, $Co(CNS)_2$ 4 pico and $Ni(CNS)_2$. 4 pico, in the region investigated.

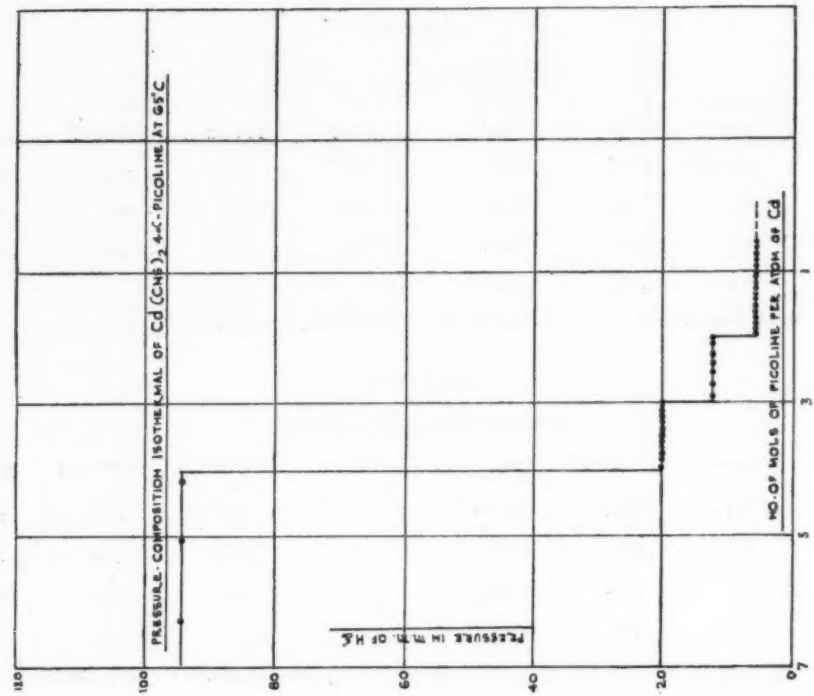


FIG. 2

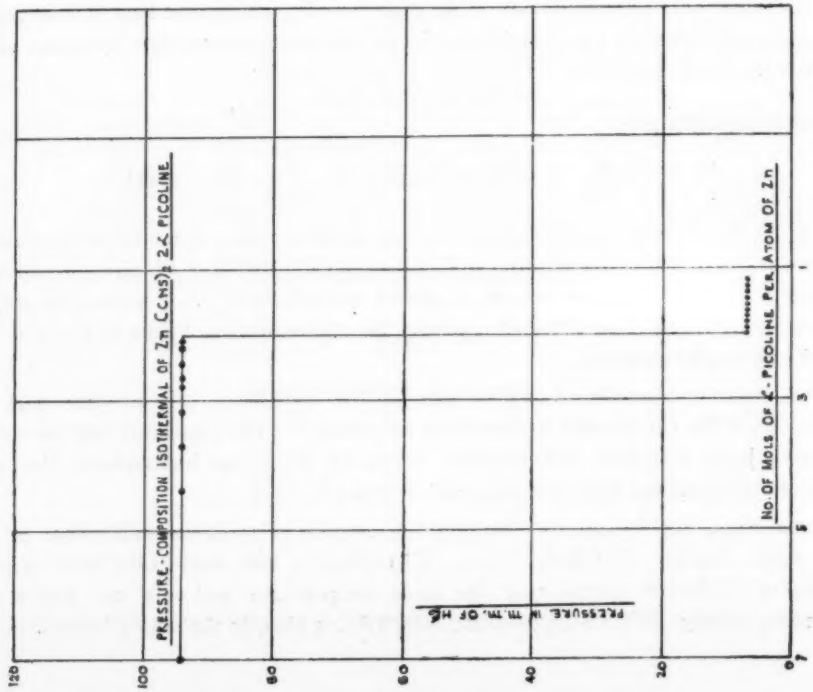


FIG. 1
At 60°.

FIG. 4

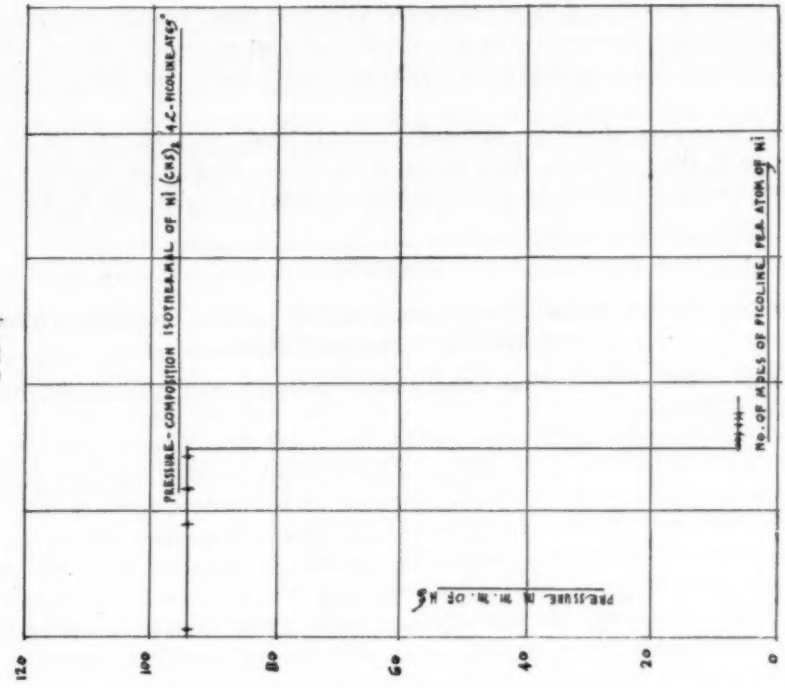
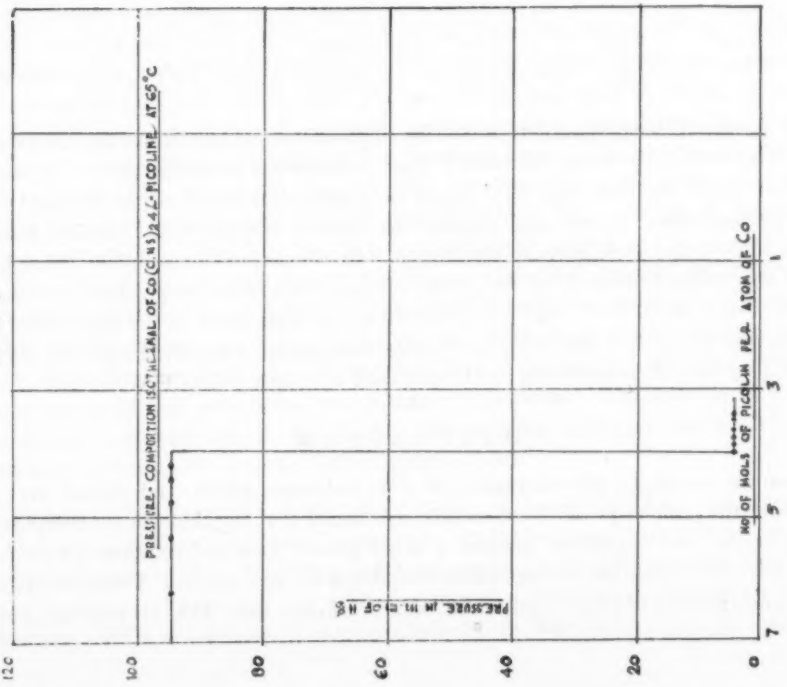

PRESSURE - COMPOSITION ISOTHERMAL OF Ni(CNS)2 4 α-PICOLINE AT 65°
PRESSURE IN m.m. OF Hg
NO. OF MOLS OF PICOLINE PER ATOM OF Ni
120
100
80
60
40
20
0
1
3
5
7

FIG. 3


PRESSURE - COMPOSITION ISOTHERMAL OF Co(CNS)2 4 α-PICOLINE AT 65°C
PRESSURE IN m.m. OF Hg
NO OF MOLS OF PICOLINE PER ATOM OF Co
120
100
80
60
40
20
0
1
3
5
7

The heat of formation of these complexes have also been directly determined by thermochemical measurements. The type of calorimeter set up and the method followed have been described in a previous paper (Sinha and Bhattacharya, this *Journal*, 1950, **27**, 22).

From these data and those obiained previously (*ibid.*, 1953, **30**, 715) for the heats of solution of the individual thiocyanates in $6N$-H_2SO_4, the heats of formation of the complexes can be calculated by the application of Hess's law (vide this *Journal*, 1955, **32**, 321).

TABLE IX

Heat of reaction of $Zn(CNS)_2$. 2 pico, $Cd(CNS)_2$. 4 pico, $Co(CNS)_2$. 4 pico *and* $Ni(CNS)_2$. 4 pico in $6N$-H_2SO_4.

Average value of the thermal capacity of the apparatus with 150 c.c. sulphuric acid = 158.0 cals. per degree.

Substance.	Wt.	Temp. (corr.)	Heat of reaction per G.F.W. (q_1).	Mean q_1.	Heat of formation (in cals. per G.F.W.).
$Zn(CNS)_2$. 2 pico	1.5800 g.	0.040°	+1,470		
	1.5211	0.038°	+1,451	+1,464	+17,632
	1.5811	0.040°	+1,471		
$Cd(CNS)_2$. 4 pico	1.0992	0.045°	+3,890		
	1.2938	0.055°	+4,036	+4,012	+30,158
	1.1261	0.050°	+4,110		
$Co(CNS)_2$ 4 pico	1.0810	0.092°	+7,355		
	1.1521	0.099°	+7,435	+7,338	+32,902
	1.1021	0.092°	+7,224		
$Ni(CNS)_2$. 4 pico	0.7155	0.038°	+4,585		
	1.4100	0.070°	+4,295	+4,429	+34,792
	1.2562	0.064°	+4,409		

The heats of formation determined by thermochemical measurements are found to agree fairly well with those calculated from dissociation pressure values. It must be mentioned, however, that the total heats of dissociation could not be obtained for all the complexes, since it was not possible to remove the whole of α-picoline from the complex under the experimental conditions. In the case of the complex [Cd. 4 pico]-$(CNS)_2$, the value obtained for the heat of formation from thermochemical measurements is 30,158 cal./G.F.W. and is practically of the same order as the sum of the heats of dissociation of 4/3, 3/2 and 2/0 α-picolinated complexes, namely, 10,341 cal., 12,534 cal. and $2 \times 7,242$ cal. respectively, making a total of 37,369 cal./G.F.W.

DISCUSSION

When the complexes of thiocyanates of zinc, cadmium, cobalt and nickel are compared with the sulphates of these metals, it is found that the thiocyanate complexes of both α-picoline and quinoline possess a much greater heat of formation and are consequently more stable than the corresponding complexes of the sulphates. These results agree with the observation of Chang and Yü (*Z. anorg. Chem.*, 1939, **243**, 14) that an increase

in the valency of the anion decreases the tendency of bivalent metals to form co-ordination compounds. The retarding effect of the sulphate ion in complex formation is also supported by the facts that the sulphates of zinc, cadmium, cobalt and nickel form complexes with quinoline or α-picoline with extreme slowness and that the presence of water is necessary for the stabilisation of these complexes. Ephraim (*Ber.*, 1920, **53B**, 548) has suggested that the presence of neutral addenda, like H_2O, stabilises the structure of the crystal by filling its seams. It is likely that the effect of the SO_4^{2-} ion, which tends to oppose the formation of complexes with quinoline or α-picoline due to unequal pairing of the anion and cation, is neutralised by co-ordination with water molecules.

The stability of a complex compound depends on several factors, but the chief among these are: (*a*) the atomic volume of the central atom, (*b*) the relative sizes of the anion and the cation, (*c*) the strength of acid and (*d*) the spatial arrangement. Ephraim (*Ber.*, 1918, **51**, 644) and Clark (*Amer. J. Sci.*, 1924, **7**, 1) have shown that when the anion is particularly large, the additive capacity of the cation for negative substance is much greater than it normally is. Necolaev and Rubinshtein (*Bull. Acad. Sci., U.S.S.R.*, 1940, 787) have stated that the stability of the complex ammines is proportional to the radius of the anion. Ephraim (*loc. cit.*) has also found that besides the relative size of the anion and the cation, spatial consideration is a controlling factor in complex formation. Ephraim has also shown ((*Ber.*, 1913, **46**, 3103) that salts of stronger acids unite more firmly with ammonia than do the salts of weaker acids. The difference of volume between the cations and the sulphate ion in the case of the metals, *e.g.* zinc, cadmium, cobalt and nickel, is greater than that between the cations and the thiocyanate ion. It would therefore be expected that the cation would be able to take up a larger number of ligand molecules in presence of the sulphate ion than when thiocyanate ion is present. The experimental results are, however, contrary to expectation. It seems that the spatial arrangement of atoms in the anion is a more important factor in complex formation than the difference in the size of anion and cation. While the sulphate ion possesses a tetrahedral structure, the thiocyanate ion is linear. It appears that in the process of crystallisation the tetrahedral sulphate ions occupy most of the available space around the metal atom, squeezing out the ligand molecules. It will be seen that although sulphuric acid is a stronger acid than thiocyanic acid, the sulphates of the bivalent metals, studied, all take up lesser number of molecules of α-picoline or quinoline than their corresponding thiocyanates. The effect of the atomic volume of the central metallic atom in complex formation is now more or less definitely established, but it is not certain what is exactly the effect of the atomic volume of the central atom in the anion. The stability of a complex must depend not only upon the atomic volume of the metal but also upon that of the central atom of the anion and its spatial configuration.

The heats of dissociations of $[Zn.2pico](CNS)_2$ $[Cd.4pico](CNS)_2$, $[Co.4pico](CNS)_2$ and $Ni.4pico(CNS)_2$ are 8,244 cals., 10,341 cals., 13,245 cals. and 11,005 cals. per molecule of α-picoline respectively. The Born and Haber cycle, deduced from the First Law of Thermodynamics, shows that the lattice energy of a crystal is dependent on its heat of dissociation. Biltz and Grimm (*Z.anorg. Chem.*, 1925, **45**, 63) have shown that complex

formation is closely connected with the nature of the crystal-lattice energy of the compounds forming the complex. They have found that the lattice energy of the ammoniates is the sum of the lattice energy of the ammonia-free salt and the heat of formation of the ammoniate. According to Yatsimirski (*Invest. Akad. Nank.*, 1945, 590) the lattice energies of $Zn(CNS)_2$, $Cd(CNS)_2$, $Co(CNS)_2$ and $Ni(CNS)_2$ are 626, 581, 616 and 627 k cals./mol. respectively. The heats of formation of [Cd.4pico] $(CNS)_2$, [Co.4pico] $(CNS)_2$ and [Ni.4pico] $(CNS)_2$ are 30,158, 32,902 and 34,792 calories/G.F.W. respectively. It is evident that the lattice energy of crystals of cobalt and nickel complexes of α-picoline is greater than that of cadmium. The present investigation further supports the findings of Biltz and Grimm (*loc.cit.*) that the increase in the lattice energy for the same number of ammonia molecules in salts of different cations having the same number of external electrons is greater, the higher the charge and smaller the radius of the cation. Cobalt and nickel α-picoline-thiocyantes possess greater lattice energies than the corresponding cadmium complex as the radii of the former two cations, 0.82Å and 0.78Å° respectively, are smaller than that of cadmium, viz., 1.03Å.

It is generally found that the heat of dissociation of the complex, which contains the highest number of ligand molecules, is lower than the one which has a smaller number of molecules attached to it, or in other words, the stability of the complex containing the lowest number of ligand molecules is the greatest, having the highest heat of dissociation. In the case of picolinated complex of cadmium thiocyanate, however, it will be observed that for the highest picolinated complex, the heat of dissociation per molecule of α-picoline is 10.34 k cals., for the next complex it is 12.55 k cals., but for the lowest complex containing 2 mols. of α-picoline it is 7.24 k cals. per mol. of picoline. No satisfactory explanation can be offered for this anomalous behaviour. It may be mentioned, however, that similar anomalous behaviour has been obtained by previous workers. Davis and Betchelder (*J. Amer. Chem. Soc.*, 1930, **52**, 4069) determined the heats of dissociation of $Co(CNS)_2.4Py$, $Co(CNS)_2.2Py$, and Davis and Ou (*ibid.*, 1934, **96**, 1061) those of $Co(CNO)_2.4Py$ and $Co(CNO)_2.2Py$ and found the values 10.73 k cals., 9.42 k cals. 16.09 k cals. and 10.15 k cals. respectively. It cannot therefore be asserted that the heat of dissociation or the stability of the complex having the least number of ligand molecules is the greatest.

Although a large amount of work has been carried out on complex compounds, it is only comparatively recently that systematic quantitative investigations have been made to determine the influence of the cation, anion and the ligand on complex formation. It is clear that the stability of the complex is the resultant of all the forces operating. Further quantitative measurements of the stability of complex compounds are necessary, especially in view of the conflicting results recorded in literature, before any comprehensive theory of complex formation can be put forward.

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STUDIES IN INDIGOID DYES. PART XV. THIOINDIGOID DYES DERIVED FROM NAPHTHALENE-2.7-DISULPHONIC ACID

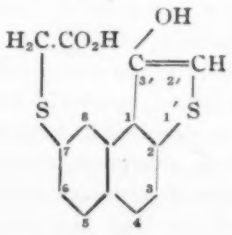
By Paresh Chandra Dutta and Dasrath Mandal

2:1-Naphtho-(3'-hydroxy-1'-thiophene)-7-thioglycollic acid, (I), has been prepared from naphthalene-2:7-disulphonic acid and condensed with various *o*-diketones, and the corresponding thioindigoid dyes obtained with a view to studying colour in its relation to chemical constitution.

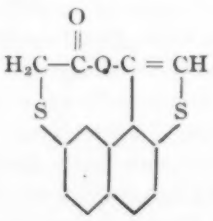
An attempt has been made for the preparation of *bis*-thioindigoid dyes from naphthalene-2:7-disulphonic acid through the *bis*-thioindoxyl and its subsequent condensation with *o*-diketones. Naphthalene-2:7-disulphonic acid was therefore first converted into its disulphochloride and then to dimercaptan by reduction, following Corbellini and Albeugs' method (*Gazzetta*, 1931, **61**, 111); the dimercaptan was converted into dithioglycollic acid and this acid through its acid chloride was cyclised by anhydrous aluminium chloride to prepare the *bis*-thioindoxyl. As has already been observed in the case of diphenyl-4:4'-dithioglycollic acid (this *Journal*, 1955, **32**, 339) and naphthalene-1:5-dithioglycollic acid (Corbellini *et al.*, *loc. cit.*), the cyclisation takes place, in this case also, with one thioglycollic acid side-chain, the other remaining unaffected. It may be that the thioindox l(I) with its thioglycollic side-chain forms immediately the lactone (II), as has already been pointed out, and thus further cyclisation is prevented, resulting in the formation of monothioindoxyl-thioglycollic acid instead of the expected *bis*-thioindoxyl.

The thioindoxyl-thioglycollic acid (I), thus obtained, has been condensed with various *o*-diketones and the corresponding indigo-thioglycollic acids (IV) were prepared. This indoxyl dissolved in dilute caustic soda, forming a greenish solution from which the *bis*-indigo sodium salt (III) was partially separated, because of its solubility in alkali, on the addition of potassium ferricyanide. The alkaline filtrate when acidified produced a dark chocolate precipitate of the *bis*-indigo-thioglycollic acid which dissolved in nitrobenzene with a deep chocolate colour. The dyes are insoluble in alcohol, slightly soluble in acetic acid and fairly soluble in nitrobenzene. They dissolve slightly in warm caustic soda solution ; in alkaline hydrosulphite they produce a yellow solution from which the original dyes are reproduced by oxidation with air. In concentrated sulphuric acid they dissolve producing a characteristic colour.

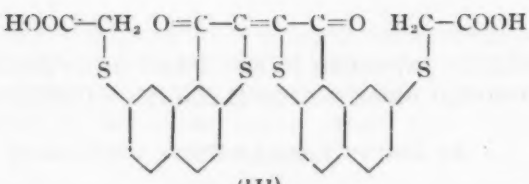
The structures of these dyes may be represented by the following formulae.



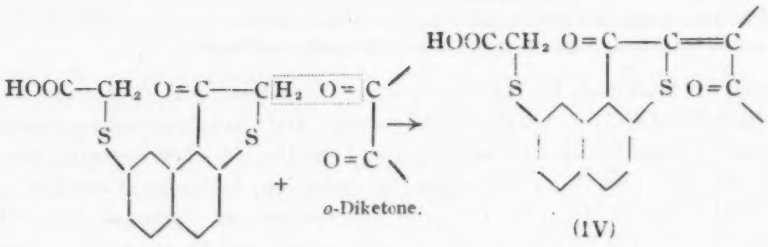
(I)



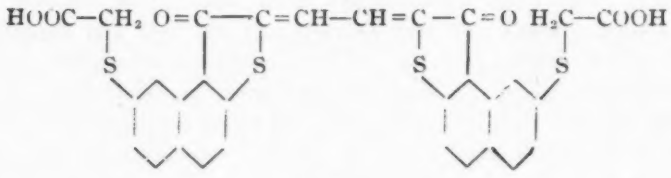
(II)



(III)



(IV)



(V)

EXPERIMENTAL

Naphthalene-2 : 7-dithioglycollic Acid.—Naphthalene-2:7-dithiol (3 g.) was dissolved in caustic soda solution (20 c.c., 10 %) and to the filtrate monochloroacetic acid (3 g.), previously neutralised with caustic soda solution, was added and the mixture heated on a water-bath for an hour. The filtrate after separating from a little gelatinous precipitate was cooled and acidified with HCl when thioglycollic acid separated out as a voluminous white precipitate. This was filtered, washed and purified by dissolving in sodium bicarbonate solution, filtering and precipitating with HCl. It was recrystallised from dilute alcohol as colorless needles, m.p. 186-87°. (Found: C, 54.41 ; H, 4.01. $C_{14}H_{12}O_4S_2$ requires C, 54.54; H, 3.9 per cent).

2:1-*Naphtho-(3′-hydroxy-1′-thionaphthene)-7-thioglycollic Acid* (I).—The preceding acid (4 g.) was suspended in petroleum ether (40 c.c., b.p. 60°-80°) and to this PCl_5 (6 g.) and pyridine (2 drops) were added and the mixture refluxed for an hour. The clear solution was then transferred by decantation from a little undissolved sticky solid and cooled in a refrigerator, when an oil, first separated, gradually solidified to white flakes, m.p. 70-71°. These after filtration were dissolved in fresh petroleum ether (50 c.c.) and treated with finely powdered anhydrous aluminium chloride (4 g.) in portions, and refluxed on a water-bath till the evolution of hydrogen chloride had ceased. After cooling, the petroleum ether was poured out, ice and HCl (conc.) were added to the chocolate-red complex, when gradually the substance became a

yellowish white mass. This was filtered and washed with HCl and water. This thioindoxyl dissolved in hot caustic soda solution with a greenish colour and was precipitated by HCl as a white curdy precipitate, which, when kept exposed to the air, became reddish due to oxidation. It could not be obtained in a very pure condition because of its susceptibility to oxidation. For condensation with various *o*-diketones, the acetic acid solution of the impure sample has been used.

bis-2:1-*Naphthothioindigo-7:7'-dithioglycollic acid* (III) was prepared by dissolving the above thioindoxyl in dilute caustic soda and adding a solution of potassium ferricyanide to the alkaline filtrate. The dark coloured sodium salt, which was fairly soluble unlike the diphenyl compound described in the previous paper, remained mostly in solution, and the free acid was obtained from it by acidifying the filtrate as a dark chocolate precipitate. This precipitate can be redissolved in alkali and reprecipitated by acids. It was crystallised from nitrobenzene as a dark chocolate mass, m.p. above 300°. It dissolves in alkaline hydrosulphite with a brown colour and dyes cotton in blue shade. It dissolves in H_2SO_4 (conc.) with a green colour. (Found: C, 57.93; H, 2.91. $C_{28}H_{16}O_6S_4$ requires C, 58.33; H, 2.77 per cent).

TABLE I

[NTA stands for naphtho-2:1-thiopheno-7-thioglycollic acid]

Indigos.	*o*-Diketones.	M.P.*	Colour & crys. shape.	Colour in H_2SO_4.	Shade on cotton.	Mol. formula.	Analysis. Found.	Calc.
NTA-3'-(5':7'-dinitro)-indol-indigo (IVb)	5:7-Dinitro-isatin	>310°	Dark chocolate powder	Green	Chocolate brown	$C_{22}H_{11}O_6N_3S_2$	N, 8.5%	8.23%
NTA-3'-(5'-bromo)-indol-indigo (IVc)	*m*-Bromo-isatin	>300°	Violet mass	Brownish violet	Pinkish violet	$C_{22}H_{12}O_4NS_2Br$	C, 53.37 H, 2.51	53.0 2.4
NTA-2'-acenaphthylene-indigo (IVd)	Acenaphthenequinone	>310°	Vermillion-red ppt.	Bluish green	Pinkish red	$C_{26}H_{14}O_4S_2$	C, 69.2 H, 3.2	68.72 3.08
NTA-2'-(5' or 6'-nitro)-acenaphthylene-indigo (IVe)	5 Nitroacenaphthenequinone	>300°	Reddish brown mass	Dark green	Greenish grey	$C_{26}H_{13}O_6NS_2$	C, 62.81 H, 2.72	62.52 2.6
NTA-2'(5':6'-dinitro)-acenaphthylene-indigo (IVf)	5:6-Dinitro-acenaphthenequinone	>305°	Chocolate-red mass	Do	Chocolate	$C_{26}H_{12}O_8N_2S_2$	C, 57.52 H, 2.23	57.35 2.2
NTA-9'-phenanthene-indigo (IV g)	Phenanthrenequinone	>300°	Dark violet mass	Dark with greenish tinge	Violet	$C_{28}H_{16}O_4S_2$	C, 70.42 H, 3.28	70.0 3.3
NTA-1'-aceanthrylene-indigo (IVh)	Aceanthraquinone	>300°	Deep brown mass	Dark green	Copper-red	$C_{30}H_{16}O_4S_2$	C, 71.65 H, 3.20	71.42 3.17

* Crystallised from nitrobenzene.

Naphtho-2:1-thiopheno-7-thioglycollic acid-3'-indol-indigo (IV).—Isatin was dissolved in acetic acid and to this an acetic acid solution of (I) was added and the mixture heated when immediately the orange-red solution became blood-red and a red precipitate began to separate out. HCl (conc., 0.5 c.c.) was then added to the mixture and boiled

for 15 minutes more to ensure complete reaction. The mixture was filtered hot, residue washed with acetic acid and alcohol and crystallised from nitrobenzene as a pinkish red powder, m.p. above 310°. It dissolves in H_2SO_4 (conc.) with a violet colour and dyes cotton from deep yellow hydrosulphite vat in red shade. (Found : C, 63.4 ; H, 3.0. $C_{22}H_{12}O_4NS_2$ requires C, 63.0 ; H, 3.1 per cent).

Preparation and properties of other naphtho-2 : 1-thiopheno-7-thioglycollic acid-indigos from compound (I) and the corresponding *o*-diketones are shown in Table I.

bis-*Naphtho*-2:1-*thiopheno*-7-*thioglycollic acid-ethylene-indigo* (V) was prepared by adding an aqueous solution of glyoxal sodium bisulphite to an alcoholic solution of (I) and boiling the mixture for an hour with the previous addition of HCl (conc. 5 c.c.). It was crystallised from nitrobenzene as a blackish brown crystalline mass, m.p. above 300°. It dissolves with a dark colour having greenish tinge and dyes cotton from a pink vat in deep violet shade. (Found : C, 60.12 ; H, 3.2. $C_{30}H_{18}O_6S_4$ requires C, 59.8 ; H, 3-0 per cent).

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STUDIES IN THIAZOLES. PART I

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2-Hydroxy- and 2-chlorothiazoles have been prepared in excellent yields.

2-Hydroxy- and 2-chlorothiazoles were required for synthesis of thiopegan derivatives and other thiazole derivatives with a view to testing their therapeutic properties.

The 2-hydroxythiazoles have been prepared by Marchesini (*Gazzetta*, 1893, **23**, 442) from α-haloketones and ammonium thiocarbamate. Tcherniac (*Ber.*, 1892, **25**, 2608), Hantzsch (*Ber.*, 1927, **60**, 2537) and Arapides (*Annalen*, 1888, **249**, 15) have converted various α-thiocyanoketones into 2-hydroxythiazoles by treating the former with dilute alkalies or acids. Ganpathi *et al.* (*Proc. Ind. Acad. Sci.*, 1946, **22**, 374) obtained 40% yield of 2-hydroxy-4 : 5-dimethylthiazole along with a major part of an oily product by boiling a mixture of α-thiocyanoethylmethyl ketone with a mixture of glacial acetic acid and concentrated sulphuric acid. They seem to have overlooked the fact that water is an essential item in the conversion of an α-thiocyanoketone into a 2-hydroxythiazole, because the reaction evidently proceeds through cyclisation of an intermediate amide (Adams, "Organic Reactions", Vol. VI, pp. 377-78). Besides, the experimental conditions were rather drastic.

While the method of Arapides (*loc. cit.*) furnished 2-hydroxy-4-phenylthiazole by prolonged treatment of ω-thiocyanoacetophenone with aqueous hydrochloric acid, ω-thiocyano 4-chloroacetophenone was recovered unchanged by us even on boiling in alcoholic-aqueous hydrochloric acid for 12 hours.

However, on heating solutions of the various ω-thiocyanoketones in glacial acetic acid in presence of concentrated sulphuric acid (0.1 c.c. for each g. of the thiocyano compound) and a small amount of water on a water-bath for about one hour, the corresponding 2-hydroxythiazoles were obtained in good yields. Moreover, these hydroxythiazoles, generally, were sufficiently pure for the purpose of further condensations.

2-Chlorothiazoles were prepared by the previous workers by diazotisation of the corresponding aminothiazoles, or the replacement of the hydroxyl group of the corresponding hydroxythiazole by treatment with $POCl_3$ (Ganpathi *et al.*, *loc. cit.*). Comparatively less known, but cheaper, method is to treat the α-thiocyanoketones with dry hydrogen chloride (Tcherniac, *J. Chem. Soc.*, 1919, **115**, 1072 ; Ganpathi *et al.*, *loc. cit.*, p. 376). But with this method Tcherniac obtained simultaneously a mixture of 2-hydroxy-4-methylthiazole and 2-chloro-4-methylthiazole from thiocyanoacetone. Georgy and Mathes (*J. Amer. Chem. Soc.*, 1952, **74**, 1719) also obtained a mixture of 2-chloro-4 : 5-dimethylthiazole and the corresponding 2-hydroxythiazole from α-thiocyanoethylmethyl ketone.

We have, however, developed this method in detail and have obtained almost quantitative yields, invariably, of the corresponding 2-chlorothiazoles. The chlorothiazoles in some cases separated out in the form of their unstable hydrochlorides which on treatment with water or weak alkali yielded free 2-chlorothiazoles, and in other cases free chlorothiazoles were obtained without the intermediate formation of the hydrochlorides. The chlorothiazoles, thus obtained, were sufficiently pure for further work. When the dry ethereal solution of ω-thiocyanoacetophenone was saturated with dry hydrobromic acid gas, a solid, presumably the hydrobromide of m.p. 217° (decomp.), was obtained. The attempted isolation of the free 2-bromo-4-phenylthiazole by treatment of the hydrobromide with aqueous sodium bicarbonate solution, however, afforded 2-hydroxy-4-phenylthiazole through hydrolysis.

EXPERIMENTAL

Preparation of the Thiocyanoketones.—The thiocyanoketones from the corresponding haloketones were invariably obtained by warming an alcoholic solution of the haloketones to 50°-60° and by the addition of a slight excess of hot saturated aqueous solution of potassium thiocyanate. The mixture was warmed for about 10 minutes and kept at the room temperature for 2 to 3 hours. The thiocyanoketones, thus formed, were isolated by the addition of water to the mixture and crystallised from dilute alcohol. The yields of the various thiocyanoketones (as obtained by these condensations, *i.e.*, without crystallisation, nevertheless they were pure enough for further work) are as recorded below.

TABLE I

ω-Thiocyano-*p*-chloroacetophenone	93.0%
ω-Thiocyano-*p*-bromoacetophenone	87.0
ω-Thiocyano-*p*-methylacetophenone	86.0
ω-Thiocyano-*p*-methoxyacetophenone	92 0
Thiocyanobenzoin	32.0
* Thiocyanoacetocatechol	80.0

(Prepared in presence of sodium iodide (1 mol.), m.p. 172-73°. Dziergowski, *Ber.*, 1894, **27**, 1987, gives m.p 147-50°.

Preparation of 2-Hydroxythiazoles.—To a solution of 2 g. of the thiocyanoketone in minimum amount of hot glacial acetic acid, 1 c.c. of water was added. This was followed by the addition of 0.25 c.c. of concentrated sulphuric acid and heated on a water-bath. The hydroxythiazole, usually light pale in colour, started separating within 5 to 10 minutes of the addition of the acid. The reaction mixture was warmed for about 1 hour to complete the reaction and then diluted with about 25 c.c. of water. The product was collected on suction. The compounds obtained were sufficiently pure for further work. However, all of them have been crystallised from alcohol (Table II).

Preparation of 2-Chlorothiazoles.—Requisite amount of the powdered thiocyanoketone was taken in the form of a suspension or solution in ether, which was cooled to 10° to 15° and saturated with dry HCl gas during 1½ to 2 hours. It was interesting to note that during the passage of the HCl gas the suspension became practically a clear solution, followed after sometime by the precipitation of the solid thiazole or its hydrochloride (Table II).

TABLE II

Preparation of 2-hydroxythiazoles.

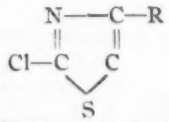
Thiocyanoketone.	Amount of acetic acid.	Thiazole obtained.	Yield of the crude product.	M.P. of crude product.	M.P. after crystallisation from alcohol.	Analysis. Found.	Calc.
ω-Thiocyano-*p*-chloro-acetophenone.	8 c.c.	2-Hydroxy-4-*p*-chlorophenyl-thiazole	97 5%	218-21°	220-22°	S: 14.81	15.1
ω-Thiocyano-*p*-bromo-acetophenone.	8	2-Hydroxy-4-*p*-bromophenyl-thiazole	90.5	235-39°	240°	N: 5 25	5.47
ω-Thiocyano-*p*-methyl-acetophenone	8	2-Hydroxy-4-*p* tolylthiazole	90.0	210-15°	220°	S: 16 75	16.54
ω-Thiocyano-*p* methoxy-acetophenone	10	2-Hydroxy-4-*p*-anisylthiazole	82.5	190-95°	195°	N: 6.45	6.71
ω-Thiocynoacetylcatechol	7	* 2-Hydroxy-4-(3 :4-dihydroxy-phenyl)-thiazole	74.0	190-205°	210°	N: 6 35	6 7
ω-Thiocyanobenzoin	6	2-Hydroxy-4 :5 diphenythiazole	82.5	220°	249-50°	S: 12.35	12.6

For each experiment 2 g. of the thiocyanoketone, 0.25 c.c. of conc. sulphuric acid and 1 c.c. of water were taken.

* This compound was found to be very soluble in acetic acid; hence it was also prepared by boiling a solution of 2 g. of the thiocyanoacetocatechol in 150 c.c. of water and 4 c.c. of hydrochloric acid for two hours, followed by concentration. The product (1.9 g.) had m.p 205-207°.

TABLE III

Preparation of 2-chlorothiazoles.



(R = various group).

No.	Thiocyanoketone.	Thiocyano-ketone taken.	Amount of ether.	Product.	Yield of crude product.	M P. of crude product.	M.P. after crystallisation	Analysis. Found.	Calc.
1	ω-Thiocyano-acetophenone	10 g.	200 c.c.	2-Chloro-4-phenyl-thiazole	81.7%	48-50°	50-51°	S, 16.7	16.41
2	ω-Thiocyano *p*-chloro-acetophenone	5	100	2-Chloro-4-(*p*-chloro-phenyl)-thiazole	86.8	96-97°	99-100°	N, 5.95	6.06
3	ω-Thiocyano-*p*-methyl-acetophenone	8	150	2-Chloro-4-*p*-tolyl-thiazole	85.7	81-82°	82°	Cl, 17.3	16.9
4	ω-Thiocyano-*p*-methoxy-acetophenone	5	300	2-Chloro-4-(-*p*-methoxy-phenyl)-thiazole	60	94-96°	96-97°	N, 6.0	6.2
5	ω-Thiocyano-*p*-bromo-acetophenone	8.5	100	2-Chloro-4-(*p*-bromo-phenyl)-thiazole	82	107-108°	110°	N, 6.1	5.8

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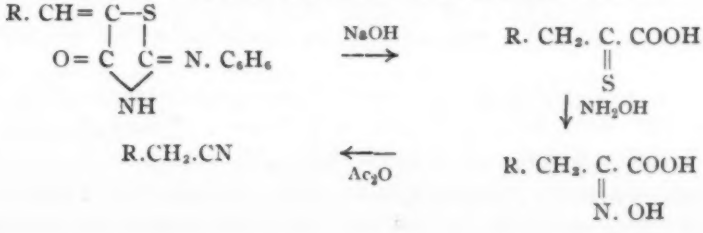
PREPARATION OF QUINOLYL-AND NAPHTHYL-THIOPYRUVIC ACIDS AND THEIR CORRESPONDING NITRILES

By H. K. Pujari and M. K. Rout

2-Phenylimino-4-thiazolidone, prepared according to the modified method (this *Journal*, 1954, **31**, 701) has been utilised for synthesis of compounds like thiopyruvic acids and their nitriles, in order to provide easy and convenient routes for the synthesis of different types of useful substances.

In the course of our studies on thiazolidones and their useful applications (this *Journal*, 1954, **31**, 701; *J. Sci. Ind. Res.*, 1953, **14B**, 16), it appeared to us worth while to attempt if reactions of thiazolidones could be employed for synthesis of different groups of chemical substances. Condensation reactions of aldehydes with rhodanine have been worked out by Granacher (*Helv. Chim. Acta*, 1922, **5**, 610; 1923, **6**, 458) and several other workers. Through condensation of rhodanine with homocyclic aldehydes, the corresponding homonitriles have been prepared in excellent yields by Julian and Sturgis (*J. Amer. Chem. Soc.*, 1935, **57**, 1126) and Cambell and McKail (*J. Chem. Soc.*, 1948, 1251). By a similar condensation of 2 : 4-thiazolidine-dione with homo- and heterocyclic aldehydes and subsequent cleavage with alkali, the corresponding thiopyruvic acids have been obtained. A similar investigation with 2-aryliminothiazolidone compounds, which may not exhibit the same tendency for ring-fission as thiazolidine-diones, does not seem to have been undertaken. We therefore considered it of interest to examine the behaviour of thiazolidones towards these condensation reactions and to ascertain, in particular, the point of ring-fission. The choice of aldehydes was limited to only a few of those which were expected to ultimately lead to production of new compounds.

Phenyliminothiazolidone, prepared by our own modified method (*loc. cit.*), was initially condensed with three different aldehydes (8-hydroxy-7-aldehydoquinoline, 8-hydroxy-5-aldehydoquinoline, 2-hydroxy-1-naphthaldehyde) and the resulting compounds were hydrolysed by alkali when substituted thiopyruvic acids were produced. These thiopyruvic acids were converted into oximino compounds by treatment with hydroxylamine hydrochloride in presence of sodium ethoxide. The oximino compounds on treatment with acetic anhydride yielded the corresponding nitriles which in turn provided simple and very convenient routes for synthesis of β-substituted ethylamines and substituted acetic acids. Preparation of nitriles has been undertaken since these will find use in our subsequent studies on synthesis of compounds related to natural products. The scheme of reactions may be formulated as shown below.



EXPERIMENTAL

5-Aldehydo (and 7-aldehydo)-8-hydroxyquinolines were prepared by the method of Sen and Ray (this *Journal*, 1932, **9**, 179) by heating a mixture of 8-hydroxyquinoline (15 g.), $CHCl_3$ (14 g.), alcohol (60 c. c.) and NaOH (16.5 g. in 30 c. c. of water) on a water-bath for 10 to 12 hours. After driving off the alcohol and excess of chloroform and then extracting once with ether to remove unchanged hydroxyquinoline, the brick-red solid was extracted with chloroform. The chloroform solution furnished the desired product, 7-aldehydo-8-hydroxyquinoline. The residue after extraction with chloroform was 5-aldehydo-8-hydroxyquinoline.

2-Phenylimino-4-thiazolidone was prepared by refluxing phenylthiourea (6.4 g.), monochloroacetic acid (4.4 g.) and anhydrous sodium acetate (3.6 g.) in presence of absolute alcohol (25-30 c. c.) for 3 to 4 hours on a water-bath. On cooling, the reaction mixture was poured into water when a pale yellow precipitate was obtained. It was washed two or three times with hot water and finally recrystallised from alcohol, m. p. 175°, yield 85%. (Found: N, 14.03; S, 16.24. $C_9H_8ON_2S$ requires N, 14.58; S, 16.66 per cent).

5-(8-Hydroxy-7-quinolylidene)-2-phenylimino-4-thiazolidone (I).—2-Phenylimino-4-thiazolidone (2 g.) and 7-aldehydo-8-hydroxyquinoline (1.6 g.) were dissolved in hot glacial acetic acid (20 c. c.) and to this anhydrous sodium acetate (2.2 g.) was added and the whole was heated for 3 to 4 hours. On cooling, the reaction mixture was poured into a large volume of water; the crystals formed was filtered off and washed with small amounts of chloroform and alcohol, yield 3 g. (86% of the theory), m. p. 106°. (Found: N, 11.76; S, 8.89. $C_{19}H_{13}O_2N_3S$ requires N, 12.11; S, 9.22 per cent).

5-(8-Hydroxy-5-quinolylidene)-2-phenylimino-4-thiazolidone (II) was prepared in the above manner by condensing 5-aldehydo-8-hydroxyquinoline with 2-phenylimino-4-thiazolidone in glacial acetic acid in presence of anhydrous sodium acetate, yield 3 g. (about 85%), m. p. 190°. (Found: N, 11.80; S, 8.85. $C_{19}H_{13}O_2N_3S$ requires N, 12.11; S, 9.22 per cent).

Cleavage of 5-(8-Hydroxy-7-quinolylidene)-2 phenylimino-4-thiazolidone.—About 2 g. of (I) was heated with 20-25 c. c. of 15% NaOH under reflux over a small flame for 3 to 5 hours. The major portion of the material dissolved. The undissolved material was filtered off. The alkaline filtrate was chilled in a freezing mixture and was acidified by rapid addition of 10% HCl. The amorphous compound which separated soon settled down on standing to a crystalline powder. This was the desired compound, *8-hydroxy-7-quinolylthiopyruvic acid* (III), yield 55%, m. p. 94°. (Found: N, 5.32; S, 12.74. $C_{12}H_9O_3NS$ requires N, 5.67; S, 12.95 per cent).

When larger quantities were run for the cleavage, the yield was comparatively lowered.

8-Hydroxy-5-quinolylthiopyruvic acid (IV) was prepared in the above manner by cleavage of (II) with alkali, yield 50%, m. p. > 300°. (Found: N, 5.28; S, 12.68. $C_{12}H_9O_3NS$ requires N, 5.67; S, 12.95 per cent).

α-Oximino-8-hydroxy-7-quinolylpyruvic Acid (V).—Sodium ethoxide, prepared from 1 g. of sodium and 30 c.c. of absolute alcohol, was mixed with a warm solution of

hydroxylamine hydrochloride (3 2 g.) in water (5 c. c.). This was added to (III) (1 g.). The reaction mixture was refluxed on a water-bath for 2 hours. The excess of alcohol was removed under reduced pressure and the residue left behind was dissolved in dilute NaOH. The alkaline solution was then cautiously acidified under good cooling when the oximino compound precipitated out. It was filtered, washed several times with water and then dried in a vacuum desiccator over KOH, yield 48%, m. p. 170° (decomp.). (Found : N, 10.94. $C_{12}H_{10}O_4N_2$ requires N, 11.39 per cent).

α-Oximino-8-hydroxy-5-quinolylpyruvic acid (VI) was obtained in exactly the same way as above by the reaction of hydroxylamine with 8-hydroxy-5-quinolylthiopyruvic acid, yield 45%, m. p. > 300°. (Found : N, 10.86. $C_{12}H_{10}O_4N_2$ requires N, 11.39 per cent).

8-Hydroxy-7-quinolylacetonitrile (VII).—The oximino-acid (V, 1 g.) was treated with 15 to 20 c. c. of acetic anhydride and was heated on a water-bath when the oximino compound gradually went into solution. After refluxing for 1 hour, the acetic anhydride was removed under reduced pressure and the residue was extracted with ether. The ethereal layer was washed with sodium carbonate solution and then with water. The ethereal solution was allowed to stand over anhydrous Na_2SO_4. On evaporating off the ether, the acetonitrile compound separated out, yield 60%, m. p. 115°. (Found : N, 14.86. $C_{11}H_8ON_2$ requires N, 15.21 per cent).

8-Hydroxy-5-quinolylacetonitrile (VIII) was obtained from (VI) by reacting with acetic anhydride in the manner described above, yield 50%, m. p. > 300°. (Found : N, 14.78. $C_{11}H_8ON_2$ requires N, 15.21 per cent).

1-Aldehydo-β-naphthol was prepared by heating a mixture of β-naphthol (8 g.), $CHCl_3$ (15 c. c.), alcohol (30-40 c. c.) and a solution of NaOH (9 g. in 15 c. c.) on a water-bath at 60°-70° for 10 to 12 hours. The excess of alcohol and chloroform was distilled off. The residue was washed with boiling water two or three times and finally crystallised from alcohol, m.p. 82°, yield 70%. Heilbron and Bunbury ("Dictionary of Organic Compounds". Vol. II) also record the m. p. as 81°.

5-(2-Hydroxy-1-naphthylidene)-2-phenylimino-4-thiazolidone (IX).—To a solution of 2 phenylimino-4-thiazolidone (2 g.) and 2-hydroxy-1-naphthaldehyde (1.85 g.) in glacial acetic acid (25 c. c.) anhydrous sodium acetate (2.2 g.) was added and the whole was then heated for 3 to 4 hours. On cooling, the crude mixture was poured into a litre of water. The precipitate formed was filtered off, washed well with hot water and then with a little alcohol and ether, yield 80%, m. p. 200°. (Found : N, 7.78 ; S, 9.02. $C_{20}H_{14}O_2N_2S$ requires N, 8.09 ; S, 9.25 per cent).

2-Hydroxy-1-naphthylthiopyruvic acid (X) was prepared from the above compound (IX, 92 g.) by heating with 15% NaOH (25 c. c.) for 3 to 4 hours. On cooling, the undissolved material was filtered off and the filtrate was cooled, and under good cooling was carefully acidified with 10% HCl. The amorphous compound settled down in a crystalline form on standing, m. p. 162° yield, 50%. (Found : S, 12.83. $C_{13}H_{10}O_3S$ requires S, 13.01 per cent).

α-Oximino-2-hydroxynaphthylpyruvic Acid (XI).—The compound (X, 1 g.) was heated under reflux with a mixture containing sodium ethoxide (1 g. of sodium in 30 c.c. of absolute alcohol) and hydroxylamine hydrochloride (3.2 g. in 5 c. c. of water) on a

water-bath for 2 hours. After distilling off the excees of alcohcl, the residue was dissolved in dilute NaOH and the resulting alkaline solution was acidified with effective cooling, and was then worked up as described earlier, yield 50%, m. p. 169°. (Found: N, 5.34. $C_{13}H_{11}O_4N$ requires N, 5.72 per cent).

2-Hydroxy-1-naphthylacetonitrile (XII).—The oximino compound (XI, 0.8 g.) was heated with 15 to 20 c. c. of acetic anhydride for one hour during which the oximino compound went completely into solution. Acetic anhydride was then removed under reduced pressure and the residue was ex_{tr}acted with ether. The acetonitrile compound was isolated from the ethereal solution on evaporation, yield 65%, m. p. 125°. (Found: N, 7.12. $C_{12}H_{10}ON$ requires N, 7.61 per cent)

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USE OF THIOSEMICARBAZONES AS REAGENTS IN INORGANIC ANALYSIS AND ANTIBACTERIALS. PART II

By G. N. Mitra and S. S. Guha Sircar

Thiosemicarbazones of 8 aldehydes and ketones were tested as reagents for common metallic radicals at different p_H ranges and the resulting colour changes or formation of precipitates were noted. Precipitates were formed with Ag, Hg and Cu, and in some cases with Co and Ni. Three of these were used for the estimation of Cu, 2 each for Co and Ni. Benzalacetone derivative was found good for quantitative estimation of Cu and Co. Benzal-, anisal-, and salical-acetone derivatives were found to be highly sensitive for Cu and Co even at $1 : 10^7$ dilutions. Some of the thiosemicarbazones also gave distinct colorations with some anions as ferrocyanide, nitrite and molybdate. The antibacterial actions of some of these derivatives against *E. Coli* and *Staphylococcus aureus* were found to be of a low order.

The present communication is an extension of the investigation reported by Guha Sircar and Satpathy (this *Journal*, 1954, **31**, 450). The thiosemicarbazones of a few more aldehydes and ketones have been prepared and their utility as analytical reagents as well as their antibacterial actions have been studied.

Experimental

The thiosemicarbazones were prepared and purified by the method described in Part I (*loc. cit.*). All the compounds prepared are new.

Aldehydes and ketones used and the melting points and analytical data of the thiosemicarbazones are shown in Table I.

Table I

Aldehyde or ketone used.	M. P. of the thiosemicarbazones.	% Sulphur. Found.	Calc.
1. *p* Aminoacetophenone	179°	15.61	15.39
2. *o*-Nitrobenzaldehyde	242°	15.07	14.30
3. Isatin	205°	15.31	14 55
4. *o* Chlorobenzaldehyde	210°	16.21	15.01
5. Benzalacetone	140°	14.95	14.62
6 Furfural	148°	19.17	18.94
7. Anisalacetone	173-74°	12.28	12.86
8 Salicelacetone	186°	13.62	13 70

An 1% of solution of the reagent in rectified spirit was added dropwise to 10 drops of each of 2*N* solutions of salts of the metals arranged in their analytical order (Ag, Hg, Pb, Cu, Cd, Bi, As, Sb, Sn, Fe, Al, Cr, Co, Ni, Zn, Mn, Ca, Ba, Sr, Mg) in a series of test tubes containing 2 c. c. of an acetate buffer of p_H between 3 and 7. The formation of any precipitate or colour change in the mixture was noted, both in cold and on heating. In case where there was any precipitate, its formation was completed by further addition

of the reagent and warming the mixture on the water-bath. It was then filtered and washed, and the filtrate was tested for the cation by further addition of the reagent solution. The p_H ranges in which precipitates coagulated best were carefully noted and the precipitation was taken to be quantitative. The complexes were further washed with alcohol to free them of the reagents, and their solubility in acids, alkalies and in some organic solvents was qualitatively studied. The complexes were also decomposed by mineral acids and the liberated cations were tested by some standard reagents to ascertain the actual formation of the complex.

In case of coloured complexes different dilutions of the cation solutions were prepared and the sensitivity of the reagents for them was noted, both in solution and by spot test on a filter paper.

The reactions of some of the anions in neutral as well as in acid media were noted. The anions tested were thiosulphate, borate, chlorate, nitrite, tungstate, molybdate, ferrocyanide, ferricyanide, thiocyanate and chromate. To about 2 c.c. of the anion solution 5 drops of an 1% alcoholic solution of the reagent were added and the colour changes noted. In case of ferrocyanide, ferricyanide, chromate and nitrite, two sets of the solutions were taken in the test tubes. To one set 5 drops of glacial acetic acid and 5 drops of the reagent solution were added and to the other set only 5 drops of acetic acid were added. The change in colour, whether immediate or delayed, was noted.

Reactions of the Reagents with the Cations at different p_H (3.42-7)

The *p*-aminoacetophenone compound formed yellow precipitate with Ag, Hg^{I}, Hg^{II}, the silver complex turning black in light. Cu gave a green precipitate and Fe^{III} gave a deep red colour on standing. The precipitates were not quantitative. The *o*-nitrobenzaldehyde compound formed yellow precipitate with Ag, Hg^{I}, Hg^{II} and Cu, the first turning black in light. Precipitation was not quantitative.

The isatin compound gave an orange precipitate changing to red on standing with Ag, yellow with Hg^{I} and Hg^{II}, and a brown precipitate with Cu. The Ag and Hg precipitates were quantitative, insoluble in water but partly soluble in alcohol; the Cu-complex was not quantitative.

With the *o*-chlorobenzaldehyde compound Ag, Hg^{I} and Hg^{II} gave pale yellow and Cu, a green precipitate; none of these were quantitative. The compounds were partly soluble in water and alcohol.

The benzalacetone compound gave a yellow precipitate with Ag, Hg^{I} and Hg^{II} (the first turning black in light), green with Cu and Co, and yellowish grey with Ni. The Co and Ni complexes were flocculent at p_H 4.99, while these were more granular on heating at p_H 5.89 and quantitative in ammoniacal medium, but at p_H 7 no complex formation was noticed. The complexes were partly soluble in alcohol and hot water.

The furfural compound gave yellow precipitates with Ag, Hg^{I} and Hg^{II} (the first turning black in light), and a green precipitate with Cu. The Cu and Hg^{II} complexes were quantitative, but all of them were partly soluble in alcohol and hot water.

The precipitate with anisal compound was yellowish brown with Ag, turning black on standing, yellow with Hg^{I} and Hg^{II}, green with Cu and Co, and yellowish

grey with Ni. The Ag, Hg^{I}, Hg^{II} and Cu, and in ammoniacal solution Co and Ni complexes were quantitative. Co and Ni did not give any precipitate below p_H 4.99 and in neutral medium. All the complexes were partly soluble in alcohol, the Cu and Co complexes being almost insoluble in water.

The salicalacetone compound gave precipitates brown with Ag, yellow with Hg^{I} and Hg^{II}. (Hg^{I} complex turning yellowish grey on addition of excess reagent), green with Cu, brownish green with Co, and dirty yellow with Ni. The precipitates were not quantitative and were partly soluble in alcohol and hot water. The Co and Ni complexes were not precipitated below p_H 4.99 and neutral, and were best precipitated in ammoniacal medium.

Colour changes with the Reagents in Neutral and Acidic Media with Anions

The *p*-aminoacetophenone compound produced colour changes in acidic medium with nitrite, tungstate and molybdate, the colour after the reactions being respectively yellow (red precipitate on standing), green and blue.

With *o*-nitrobenzaldehyde compound molybdate and tungstate gave bluish and greenish yellow colour respectively in acid medium.

The isatin compound gave yellow colorations with nitrite and molybdate, and greenish yellow with tungstate in acidic solutions.

o-Chlorobenzaldehyde compound produced a yellow turbidity with nitrite and a green colour with tungstate in acidic medium.

In acid medium the benzaldehyde and furfural compounds gave a green turbidity with tungstate and the latter also imparted a bluish tinge with molybdate.

The salicalacetone compound gave yellow colorations with thiosulphate and borate, yellow turbidity with ferrocyanide and a green colour with ferricyanide in neutral medium. In acid medium it produced yellow colorations with borate and molybdate, brown turbidity with tungstate and a deep green colour with ferro- and ferricyanides.

Thiosemicarbazide itself gave a purple colour with ferrocyanide in neutral medium. In acid medium it produced turbidity of faint yellow with nitrite, blue with molybdate and green with tungstate and ferrocyanide.

TABLE II

Sensitivity of the reagents towards metallic cations.

(1 g. in c. c.).

	Serial number of reagents.							
Cation.	1.	2.	3.	4.	5.	6.	7.	8.
Cu	10^5	10^4	10^5	10^4	10^7	10^6	10^7	10^7
Hg	10^4	10^4	10^4	10^4	10^5	10^5	10^5	10^5
Co	...	...	...	...	10^7	...	10^7	10^7
Ni	...	...	...	...	10^5	...	10^5	10^5

Co and Ni complexes were studied in ammoniacal medium.

The resorcylaldehyde-thiosemicarbazone, prepared earlier by Satpathy and Guha Sircar (*loc. cit.*), was found to produce colour changes with thiosulphate, borate, nitrite, molybdate and tungstate, the colour after reaction being yellow. In acid medium it gave with chlorate and molybdate yellow colour, with nitrite reddish brown, faint purple with thiocyanate, and greenish turbidity with tungstate.

Spot test.—In case of Hg, Cu Ni and Co, a drop of the cationic solution was put on a small piece of filter paper, allowed to dry and then a drop of an 1% alcoholic solution of the reagent was placed on it. The spot was then exposed to ammoni. vapour from a bottle containing liquor ammonia. The tests may be carried out in a micro test tube.

Quantitative Estimations

Quantitative estimations could not be made with Ag and Hg complexes as they were very unstable and liable to decomposition on drying.

Cu, Co and Ni were estimated quantitatively. Sulphate solutions of Cu, Co and Ni were standardised respectively by iodimetric, pyridine and dimethylglyoxime methods.

Estimation of Cu^{2+}—The standard solution (10 c.c.) was taken in 300 c.c. beaker, an acetate buffer (100 c.c.) of p_H 5.23 was added and heated to 70°-80°. A hot 1 or 2% solution (alcoholic) of the reagent was added dropwise with constant stirring till complete precipitation. The temperature was maintained at 70°-80° for ½ hour with occasional stirring. In case of reagents 5 and 7, the precipitate was filtered while hot, and in case of No. 6, it was allowed to settle for one hour and filtered when cold. The precipitate was washed with hot water and 2% alcohol and dried at 110° to a constant weight. G-4 crucibles were used for filtration. The results assuming 2 : 1 combination between the reagent and Cu are recorded below.

TABLE III

Standard soln. taken = 10 c.c.

Reagent No.	5	6	7
Mean wt. of the complex (g.)	0.2620	0.1995	0.3054
Calc. wt. of ,,	0.2621	0.2056	0.2994

The weight in case of No. 6 was low due to a slight solubility of the complex in hot water, and that in case of No. 7 was high due to the difficulty in removing the reagent.

The structure of the Cu complex may be represented as:

$$R{=}N.NH.\underset{\underset{NH}{\|}}{C}-S-Cu-S-\underset{\underset{NH}{\|}}{C}.NH.N{=}R$$

(R = aldehyde or ketonic ligand)

A weighed amount of the Cu complex was taken in a weighed porcelain crucible and decomposed carefully by HNO_3 (1 : 1). The acid was carefully evaporated to dryness and the complex ignited to a constant weight. The differences of weights gave the weight of CuO, from which %Cu in the complex was calculated.

TABLE IV

Reagent No.	6	5	7	4
%Cu (found)	16.09	13.17	10.58	12.72
%Cu (calc.)	15.90	12.71	11.34	12.98

Estimation of Cobalt.—To the standard $CoSO_4$ solution (25 c.c.) in a 300 c.c. beaker and diluted to about 100 c.c. solid A.R.NH_4Cl (0.5 g.) was added and the contents heated to 70°-80°. Dilute NH_4OH solution (5 c.c.) was then added to the hot solution, followed by dropwise addition of 2% hot alcoholic solution of the reagent with constant stirring till complete precipitation and then left on the water-bath at 80° for 1 hour. Finally one or two drops of the reagent solution were added to test precipitation. It was then kept for further 10 minutes on the water-bath. The rest of the procedure was the same as with Cu complex. With reagent No. 5 mean wt. of the complex found was 0.1196 g. (calc. 0.1194%) and with No. 7, the mean wt. found was 0.1335% (calc. 0.1337 g.). The weights in case of reagent No. 7 were, however, slightly low or high as the complex was soluble to some extent in the wash-liquid, too little washing providing high, and too much washing, low results.

The structure of the cobalt complex, similar to that of Cu, was established by igniting to Co_3O_4 and calculating the %Co. The %Co found in case of reagent No. 5 was 11.64 (calc. 11.90%) and that in case of reagent No 7 was 10.32 (calc. 10.61%)

Estimation of Nickel.—The method of estimation was the same as in the case of cobalt, mean wt. of the complex with reagent No. 5 found was 0.2220 g. (calc. 0.2231 g.) and with reagent No. 7, 0.5002 g. (calc. 0.5002 g.). The weights were low in case of reagent No. 5 due to the solubility of the complex in the wash liquid. In case of No. 7, the weights were irregular due to the solubility of the complex in wash liquid, too much washing yielding low and too little washing, high results.

Antibacterial Action of the Thiosemicarbazones and their Mercury Complexes

Thiosemicarbazones, prepared previously as well as in the present work, were tested for their antibacterial action, by the Rideal-Walker drop method (Mickiel and Macarthy, "Handbook of Practical Bacteriology", p. 313).

The test organisms were 24 hours' cultures of *E. Coli* and *Staphylococcus aureus*, incubated and grown in nutrient broth medium at 37°. The results are recorded in Table V.

About five mercury complexes of five of the thiosemicarbazones were prepared, their structure established by determining the %Hg present in them by the usual gold crucible method and their antibacterial actions tested.

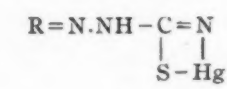
Percentages of Hg observed in some cases were high as the mercury complexes were unstable and decomposed in presence of traces of reducing agents forming black HgS.

TABLE V

Time of contact = 5 minutes.

	Thiosemicarbazone of	M.E.D. for E.Coli.	M.E.D. for Staphylo.		Thiosemicarbazone of	M.E.D. for E.Coli.	M.E.D. for Staphylo.
1.	*p*-Aminoacetophenone	1 : 2000	1 : 2000	9.	Resorcyl aldehyde	1 : 1000	< 1 : 1000
2.	*o*-Nitrobenzaldehyde	1 : 8000	1 : 10,000	10.	*p*-Nitrobenzaldehyde	1 : 4000	1 : 2000
3.	Isatin	1 : 1000	1 : 1000	11.	*m*-Nitro-"	1 : 1000	1 : 1000
4.	*o*-Chlorobenzaldehyde	1 : 2000	1 : 2000	12	Salicaldehyde	1 : 1000	1 : 1000
5.	Benzalacetone	1 : 2000	1 : 1000	13.	Cinnamaldehyde	1 : 2000	1 : 2000
6.	Furfural	< 1 : 1000	< 1 : 1000	14.	Vanillin	1 : 1000	1 : 1000
7.	Anisalacetone	< 1 : 1000	< 1 : 1000	15.	*p*-5-Methylamino-benzaldehyde	1 : 2000	1 : 4000
8.	Salicalacetone	1 : 2000	1 : 2000	16.	Thiosemicarbazide (contact 10 minutes)	< 1 : 1000	< 1 : 1000

The assumed structure of the mercury complex is shown below.



(R = aldehyde or ketonic ligand).

TABLE VI

Derivatives of	% Mercury. Found.	Calc.
p-Aminoacetophenone	49.57	49.30
Resorcyl aldehyde	49.56	48.94
Furfural	55.84	54.53
o-Nitrobenzaldehyde	46.29	47.44
o-Chlorobenzaldehyde	49.32	48.67

While testing for the antibacterial actions of the above mercury complexes, growth was observed in all cases at dilutions lower than those in which the unmercurated compounds produced growth.

From the above observations it is concluded that the thiosemicarbazones are generally not very effective against the bacteria tested, though their activity against tubercule bacillius was established by the work of Domagk.

The inactivity of the mercury complexes might be accounted for from a consideration of the structure given above. The thiosemicarbazone molecule, while combining with the Hg, utilises both its valencies forming a chelate compound and renders it incapable of fixing itself on bacterial cells.

Fildes explains the antibacterial action of mercury due to its combination with cellular metabolite containing -SH groups and thus depriving the cell of those metabolites as a result of which the cell dies (*Brit. J. Exptl., Path.*, 1940, **21**, 67). Here the thiosemicarbazones supply the -SH groups and thus inactivate the Hg atom.

Such deactivation of mercury complexes has also been reported by other workers. In glutathione the neutralisation takes place in the proportions of 1 mol. of Hg per 2 mol. of -SH and the formed product is devoid of -SH. If the concentration of -SH in glutathione is about 4 times that of mercury, growth occurs (cf. Porter, "Bacterial Chemistry and Physiology", John, Wiley & Sons, Inc., 1947, p 273).

Patnaik and Guha Sircar observed that cystein could effectively antagonise the activity of a certain number of mercurated P.A.S. derivatives (this *Journal*, 1953, **30**, 563, 583). In the present work the activity of phenylmercuric nitrate was tested with *E. Coli* and *Staphylococcus aureus* and then it was mixed with equimolecular proportion of a thiosemicarbazone and thiosemicarbazide and its activity again tested. There was a marked diminution of activity. Work in this line is in progress and will be reported in due course.

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5-ARYLIDENE-2-α-NAPHTHYLIMINO-4-THIAZOLIDONES AND SOME OF THEIR DERIVATIVES. PART I

By Bhaskar Das and M. K. Rout

Mercuration of 2-α-naphthylimino-4-thiazolidone and its arylidene derivatives (cf. Das and Rout, *J. Sci. Ind. Res.*, 1955, **14B**, 16) has been effected by treatment with mercuric acetate. The resulting acetoxymercuri compounds have been examined for their bactericidal and fungicidal actions.

In course of our studies on thiazolidone compounds (Pujari and Rout, this *Journal*, 1954, **31**, 701), it appeared to us of considerable interest to prepare some of their mercurated derivatives in view of the pronounced antibacterial action of mercury and also of the results of our investigations in this direction (Rout and Pujari, *J. Amer. Chem. Soc.*, 1953, **75**, 4057 ; Guha Sircar and Rout, this *Journal*, 1952, **29**, 779). The fungicidal activity of mercury is quite well known. The fungicidal activity in known organic sulphur fungicides like tetramethylthiuram disulphide, thiourea and thiosemicarbazide is attributed to the presence of the N—C—S group (Goldsworthy, *Phytopath.*, 1942, **32**, 497). We were therefore led to examine the effect of this N—C—S group in cyclic structures like thiazole and thiazolidone. Our investigations on mercurated thiazoles indicate that they are very powerful fungistatic agents (Rout, Pardhi and Das, *Nature*, 1954, **174**, 516). We therefore considered it worth while to study the effect of mercuration of thiazolidones on fungistatic action.

In the present communication, eleven different 5-arylidene-2-α-naphthylimino-4-thiazolidones, prepared by the reaction of 2-α-naphthylimino-4-thiazolidone with aldehydes, have been mercurated with mercuric acetate in dilute acetic acid-alcohol medium. In the acetoxymercuri compounds formed, the acetoxymercuri group is assumed to have entered the naphthyl nucleus of the naphthylimino group, in support of which the following arguments are advanced.

Table I

5-Arylidene-2-(-acetoxymercuri-α-naphthylimino)-4-thiazolidone.

No. of compounds.	Nature of aldehydes from which the arylidene nucleus is derived.	*M. P.	Yield.	% Mercury. Found.	% Mercury. Calc.	% Sulphur Found.	% Sulphur Calc.
1	Benzaldehyde	216°	75%	34.32	34.08	5 07	5.43
2	*o*-Nitrobenzaldehyde	219°	65	31.95	31.66	4 82	5.05
3	*m*-Nitrobenzaldehyde	202°	60	31.84	31 66	4.83	5 05
4	*p*-Nitrobenzaldehyde	205°	65	31.03	31.66	5.62	5 05
5	*p*-Hydroxybenzaldehyde	232°	60	32 85	33.18	4 88	5.29
6	Cinnamaldehyde	230°	65	32.27	32 64	5.72	5.20
7	Salicylaldehyde	222°	70	33 09	33 18	5.79	5.29
8	Anisaldehyde	230°	85	32.53	32.42	4.90	5.17
9	Vanillin	233°	65	31.98	31.61	5.68	5.04
10	Furfuraldehyde	216°	65	34.23	34.67	5.93	5.53
11	*p*-Dimethylaminobenzaldehyde	238°	70	31.09	31.76	4 87	5.06

* The compounds melt with decomposition.

The fact that both the parent thiazolidone and its 5-arylidene derivative can be mercurated exactly under the same conditions, giving rise to exactly similar products, rules out the possibility of acetoxymercuri group having entered the CH_2 group in 5-position of the thiazolidone nucleus. The compound is not decomposed by alkali, thus leading to the conclusion that Hg has not entered the NH group in position-3. So the only remaining position for the attachment of Hg is the arylimino group. In view of the observations made by previous workers (Newton Friend, "Text-book of Inorganic Chemistry", 1928, Vol. XI, Part I) on the mercuration of aromatic amines, it can be safely assumed that the acetoxymercuri group has entered the β-position of the naphthalene nucleus.

The bactericidal tests of these acetoxymercuri compounds were carried out as reported in previous communications (Pujari and Rout, this *Journal*, 1954, **31**, 257 ; Mahapatra and Rout, *J. Sci. Ind. Res.*, 1954, **13B**, 378). Some of the mercurated arylidene-thiazolidones were found to be active in dilutions of 1 : 50,000 against *staph. aureus* and 1 : 100,000 against *E. Coli*. The details of this investigation will be published elsewhere.

Fungicidal activity was assayed with the test fungus as reported by Pujari and Rout (*J. Sci. Ind. Res.*, 1955, **14B**, 13). These mercurated compounds were found to be very powerfully fungicidal, being 100% effective in inhibiting the spore germination of the fungus even at a concentration of 5-6 ppm. The details of fungicidal tests will be published elsewhere.

EXPERIMENTAL

The preparation of 2-α-naphthylimino-4-thiazolidone and its arylidene derivatives has been already reported (*loc. cit.*).

2-(-βAcetoxymercuri-α-naphthylimino)-4-thiazolidone.—To an alcohol- dilute acetic acid solution of α-naphthylimino-4-thiazolidone (1 g.) an aqueous solution of mercuric acetate (1.7 g.), acidified with dilute acetic acid, was added with vigorous stirring. After some time the precipitate appeared. The reaction mixture was allowed to stand overnight and then filtered. The precipitate was washed with hot water 3 to 4 times and then with very dilute acetic acid. Finally it was washed with alcohol, m.p. 205° (decomp.), yield 70%. (Found : Hg, 40.25 ; S, 6.02. $C_{15}H_{12}O_3N_2HgS$ requires Hg, 40 07 ; S, 6.39 per cent).

Benzylidene-2-(β-acetoxymercuri-α-naphthylimino) -4-thiazolidone.—5-Benzylidene-2-(α-naphthylimino)-4-thiazolidone (1.1 g.) was dissolved in alcohol-dilute acetic acid solution and to it an aqueous solution of mercuric acetate (1.4 g. in 15 c. c. of water and acidified with acetic acid) was added with vigorous stirring. After some time precipitation occurred. The reaction mixture was kept overnight to allow the precipitate to settle down and then filtered. It was purified as the preceding compound, m. p. 210° (decomp.), yield 75%. (Found : Hg, 34.32 ; S, 5.07. $C_{22}H_{16}O_3N_2HgS$ requires Hg, 34.08 ; S, 5.43 per cent).

In some cases where the compounds were not appreciably soluble in dilute acetic acid and alcohol mixture, the mercuration was effected by heating the mixture under reflux.

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ESSENTIAL OIL FROM THE SEEDS OF *AGLAIA ODOROTISSIMA BLUME*. BIJDR.

By K. K. Baslas

The essential oil from the seeds of *Aglaia odorotissima Blume*. Bijdr. contains aromadendrene as the chief constituent (approx. 50%), cineol (approx. 10%), α-terpinene (12.5%) and citral (approx. 7%) and a sesquiterpene (?).

The plant of *Aglaia odorotissima Blume*, Bijdr., known in vernacular as 'Priyangu', is indigenous to India and belongs to N.O. Meliaceae. It occurs on the hills of Mt. Abu, W. Ghats and Travancore. The root, bark and seeds are used in the Indian system of medicine. Root and bark are acrid, bitter and referigerating and are used for curing dysentery, leucoderma and other skin diseases. Seeds are acidic, cooling and astringent to the bowels. They are used for removing biliousness etc. (Kirtikar and Basu, "Indian Medicinal Plants", Vol. I, p. 551).

The essential oil prossesses the following properties: d^{20}, 0.9295; n^{20}_D, 1.5013; $[\alpha]^{20}_D$, +3°.3; acid value, 1.2; ester value, 11.2.

On distillation of the oil at a reduced pressure (15 mm.) the following fractions were obtained: (I) 62-63° (2 c.c.), (II) 64-66° (2.5 c.c.), (III) 112-113° (1.5 c.c.), (IV) 130-135° (10 c.c.), (V) 148-155° (2 c.c.); residue, 1.5 c.c.

Fraction (I) is strongly odorous and distils at 174° at atmospheric pressure. It absorbed bromine and did not show any reducing properties, nor did it show the presence of any functional groups. Its boiling point and odour suggest its identity with cineol which has been subsequently confirmed by preparing its derivatives. It forms a solid compound with syrupy phosphoric acid (Kebler, *Amer. J. Pharm.*, 1898, **70**, 1209) and a crystalline compound with resorcinol, melting at 85-87° (Baeyer and Virck, *Ber.*, 1902, **35**, 1209). On warming this product with caustic soda, the regenerated cineol obtained after fractionation boiled at 178°. The amount of cineol in the oil was estimated by treating it with a 50% solution of resorcinol and decomposing the solid addition compound with caustic soda when cineol was liberated. Estimated in this way the percentage of cineol in the oil was found to be 11%.

Fraction (II) distilled at 178-79° at atmospheric pressure. It slightly smelt of cineol and freed off the latter by treating with a solution of 50% resorcinol. The purified sample smelt slightly like that of lemons and decolorised bromine water. It did not form any nitrosochloride or nitrosate. It did not form nitrosite, prepared by the usual procedure, but yielded the derivative by following the procedure modified by Wallach (*Annalen*, 1887, **239**, 35). After recrystallisation from methyl alcohol it melted at 154-55°. Analysis of the fraction corresponds with the composition $C_{10}H_{16}$. (Found: C, 88.1; H, 11.9. Calc. for $C_{10}H_{16}$: C, 88.2; H, 11.8 per cent).

The boiling point of the fraction and the melting point of the nitrosite suggested its identity with α-terpinene which was subsequently confirmed by preparing the solid

dihydrochloride (*Annalen*, 1910, **374**, 324), maleic anhydride adduct (*J. Org. Chem.*, 1942, **7**, 402) and deriving the acid from the adduct.

Fraction (III) decomposed on being distilled at atmospheric pressure and reduced Fehling's solution and showed general reactions of an aldehyde. Its bisulphite compound was prepared by the method of Tiemann (*Ber.*, 1898, **31**, 3307) and the semicarbazone prepared directly from the bisulphite compound (Tiemann, *loc. cit.*) in presence of free acetic acid. On recrystallisation it melted at 163°. From the boiling point of the aldehyde and the melting point of its semicarbazone, it was identified as α-citral.

Fraction (IV) forms the chief fraction consisting of about 50% of the oil. It possesses the following physical properties : d^{20}, 0.9165 ; $[\alpha]^{20}_{D}$, + 2°.4 ; n^{20}_{D}, 1.4992. The analysis corresponds to the composition $C_{10}H_{16}$ as well as $C_{15}H_{24}$ (Found : C, 88.4 ; H, 11.5%). The fraction was thus identified to be a sesquiterpene, but did not form any nitrosite, nitrosate or nitrosochloride, nor did it give any hydrochloride. But the solution became violet on the passage of hydrochloric acid, suggesting the presence of aromadendrene which was subsequently confirmed by treating two drops of the fraction, dissolved in excess of glacial acetic acid, with bromine vapours, when a crimson colour was obtained which soon changed to violet and finally to indigo-blue (Guenther, "Essential Oils", Vol II, p. 111). Further confirmation was obtained by preparing oxidation derivatives, aromadendrene glycol, melting at 117-18° (Radcliffe and Short, *J. Chem. Soc.*, 1938, 1200) and aromadendrone, m.p. 84-85° (Radcliffe and Short, *loc. cit.*). The ketone, aromadendrone, was analysed and its identity established by preparing its semicarbazone (m.p. 195-96° ; Radcliffe and Short, *loc. cit.*) On dehydrogenation with sulphur a blue coloured liquid was obtained which was identified as *S*-guaiazulene by preparing its picrate (m.p. 121-22°; Pfau and Platnner, *Helv. Chim. Acta*, 1936, **19**, 876). As shown in Table I, the properties of this fraction agree closely with those of aromadendrene described in literature, and thus the presence of aromadendrene in this fraction is confirmed.

Fraction (V) distilled at 148°-152°/15 mm. on refractionation and was found to afford no solid derivatives. On being treated with bromine vapours in glacial acetic acid slight violet colour, changing to indigo-blue, was obtained, indicating the presence of a slight amount of aromadendrene in this fraction. Analysis of the fraction and determination of the molecular weight correspond with the composition $C_{15}H_{24}$. Thus, the fraction was found to contain another sesquiterpene, but its nature could not be ascertained and further examination could not be carried out on account of too small an amount of the fraction being available.

The residual liquid decomposed vigorously on attempting to distil it even at the reduced pressure (10 mm.).

Table I describes the properties of the different fractions found in the oil together with those substances which correspond to them in literature.

EXPERIMENTAL

Isolation of the Oil.—The essential oil was obtained by steam distillation of the dried seeds (20 kg.) from a copper still fitted with a copper spiral condenser. The

steam-distillate was extracted with chloroform and after drying the solvent it was evaporated on a water-bath. The yellowish oil obtained in 0.1% (20 c.c.) yield has the properties recorded in the introductory part.

Fractionation of the Oil.—The fractions obtained by distilling 20 c.c. of the oil at 15 mm. pressure and their boiling ranges are recorded in the introductory part and their properties in Table I.

TABLE I

Properties of the fractions.	Properties of corresponding substances as described in literature.
Fraction I :	Cineol :
B.P. 178°	176-77° (Gildmeister & Hoffmann, "Ethereal Oils", Vol., I,p. 665)
Resorcinol addition compoun l m.p. 85-87°	80-85° (*loc cit.*)
Fraction II :	α-Terpinene :
B.P. 178-79°	179-81° (Wallach, *Annalen*, 1906, **359**, 149)
Nitrosite m.p. 154-55°	155° (Wallach, *loc. cit.*)
Dihydrochloride m.p. 51-52°	51-52° (Wallach, *loc. cit.*)
Maleic anhydride adduct m p. 61-62°	61-62° (*loc. cit*)
Dicarboxylic acid derived from adduct, m.p. 147-48°	147-48° (*loc. cit*)
Fraction III :	α-Citral :
B.P. 112-15°/15 mm.	117-19°/20 mm. (Tiemann & Semmler, *Ber.*, 1893, **26**, 2709)
Semicarbazone m.p. 163°	164° (Tiemann, *loc. cit.*).
Fraction IV :	Aromadendrene :
B.P. 130-35°/15 mm.	122-27°/10 mm. (Radcliffe and Short, *loc. cit.*)
d^{20}, 0.9165	0.9122-0.9197 (*loc. cit.*)
$[\alpha]^{20}_D$, +2°.4	1°.4 −+15°.41 (*loc. cit.*)
Aromadendrene glycol m.p. 117-18°	118° (*loc. cit.*)
Aromadendrone m p. 84-85°	84.5-85° (*loc. cit.*)
Semicarbazone m.p. 195-96°	195-196° (*loc. cit*)

Identification of Cineol in Fraction (I)

Cineol-phosphoric Acid Addition Compound.—To the fraction (0.5 c.c.), cooled by ice and salt, was added dropwise (0.5 c.c.) syrupy phosphoric acid (*d* 1.75), similarly cooled. Thorough mixing was necessary. The addition product separated as a pasty mass which became harder on further cooling.

Cineol-resorcinol Addition Compound.—Resorcinol (0.5 g.) was added to 1 c.c. of the fraction and the mixture warmed until resorcinol went into solution. On cooling, the addition product separated in rhombic plates. On filtering with a little alcohol and drying, the compound melted at 85-86°. Several recrystallisations from alcohol raised the melting point to 87°. A mixed melting point determination with cineol-resorcinol compound from a genuine sample of cineol, isolated from the plant of *Blumea lacera*, did not show any depression.

Identification of Terpinene in Fraction (II)

Nitrosite.—To a cooled mixture of the fraction (0.5 c.c.), glacial acetic acid (0.25 c.c.) and water (1 c.c.) was added gradually a concentrated solution of sodium nitrite (0.5 g.) in water, when a reddish yellow colour appeared. On keeping and further cooling of the mixture in ice, a crystalline solid separated which was washed with water, petroleum ether and finally crystallised from methyl alcohol. After several recrystallisations it melted at 151-55°.

Dihydrochloride.—The fraction (0.5 c.c.) was dissolved in absolute ether and while the solution was cooled in a freezing mixture, hydrochloric acid gas was passed into it till saturation. The reaction product was poured on a watch-glass when a crystalline solid was obtained which on several recrystallisations from alcohol melted at 51-52°.

Maleic Anhydride Adduct.—The fraction (0.5 c.c.) was dissolved in ether and a solution of 0.5 g. of maleic anhydride, dissolved in the same solvent, was added to it and the mixture refluxed for about half an hour. On cooling, a crystalline solid separated, m.p. 58-59°. On several recrystallisations from alcohol it melted at 61-62°

Dicarboxylic Acid derived from the Adduct.—The adduct obtained above was treated with a little warm solution of caustic potash and then acidified with dilute hydrochloric acid and extracted with ether. After drying the ether extract, the solvent was distilled off and the residual solid recrystallised, m.p. 147-48°.

Identification of Citral in Fraction (III)

A cold saturated solution of sodium bisulphite was added to 1 c.c. of the fraction, kept cool by ice. On adding gradually glacial acetic acid (equivalent amount) and vigorous shaking, crystals of the bisulphit compound began to separate. These were filtered off and freed from adhering oil by pressing between filter papers and drying on a porous plate. The crystals were dissolved in excess of water, and to the solution was added a strong solution of semicarbazide hydrochloride and sodium acetate in water and glacial acetic acid. On cooling by freezing mixture and on vigorous shaking, semicarbazone separated which was filtered off, dried and recrystallised from alcohol, m.p. 163-64°. A mixed melting point determination with the semicarbazone, prepared from a genuine sample of citral (B.D.H.), showed no depression.

Identification of Aromadendrene in Fraction (IV)

Colour test.—Two drops of the fraction were dissolved in 3 c.c. of glacial acetic acid and bromine vapours were passed in the solution. On shaking a crimson colour was obtained which soon changed to violet and then finally to indigo-blue.

Oxidaton : Aromadendrene Glycol.—The fraction (6 g.) was suspended in water and cooled in ice and a 4% solution of $KMnO_4$ added together with 1 g. of caustic potash, and left overnight in the referigerator. The reaction product was steam-distilled to remove unchanged hydrocarbon and the liquid filtered off to remove manganese dioxide. The filtrate was evaporated to dryness in a current of carbon dioxide and the residue extracted with ethyl alcohol. After distilling off the alcohol, it was treated with

a little of sodium bisulphite solution, washed with water and then extracted with ethyl acetate. On evaporation of the solvent a syrupy liquid was first obtained which solidified later on. After repeated recrystallisations from ethyl acetate the substance melted at 117-18°. (Found: C, 75.2; H, 11.1. Calc. for glycol $C_{15}H_{26}O_2$: C, 75.6; H, 10.9 per cent).

Aromadendrone.—Aromadendrene glycol (0.5 g.) was dissolved in acetone and a dilute solution of 5% $KMnO_4$ added to it and the mixture kept in a referigerator overnight. A few drops of HCl were added to decolorise the excess of $KMnO_4$ and MnO_2 filtered off. The filtrate was evaporated in a current of CO_2 and the residue extracted with alcohol. After removal of the solvent a solid remained behind which after several recrystallisations melted at 84-85°. (Found: C, 81.6; H, 10.7. Calc. for $C_{14}H_{26}O$: C, 81.6; H, 10.0 per cent).

Semicarbazone of Aromadendrone.—A small amount of the ketone was dissolved in alcohol and treated with a saturated solution of semicarbazide hydrochloride and sodium acetate and kept after vigorous shaking. After about two hours crystals separated which were filtered and recrystallised from alcohol. After several recrystallisations it melted at 195-96°. (Found: N, 15.56. Calc. for $C_{15}H_{25}ON_3$: N, 15.97 per cent).

Examination of Fraction (V).—It responded to the colour test of aromadendrene, but very slight colour was obtained indicating that aromadendrene was present as an impurity. Hence, it was redistilled till the sample did not respond to the colour test. The analytical data (Found: C, 88.2; H, 11.4%) correspond to $C_{10}H_{16}$ as well as to $C_{15}H_{24}$. Molecular weight determination by freezing point method was found to be 203, while a sesquiterpene requires 204. It did not form any nitrosochloride, nitrosite, nitrosate nor any hydrochloride. Further work could not be done on account of the small quantity being available.

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REDUCTION OF CARBINOLAMINE BASES WITH SODIUM BOROHYDRIDE

By S. Bose

Reduction of carbinolamine bases like berberine, cotarnine and hydrastinine has been effected by sodium borohydride in presence of methanol or ethanol at ordinary temperature and also with $LiAlH_4$, furnishing dihydro-anhydro derivatives.

Chaikin and Brown (*J. Amer. Chem. Soc.*, 1949, **71**, 2775) first reported the use of sodium borohydride as a reducing agent. This reagent, though less reactive than lithium aluminium hydride, has some advantage over the other owing to its greater selectivity of action as well as for the convenience of working up the reaction products in homogeneous methanolic solution. According to Chaikin and Brown, sodium borohydride can smoothly reduce aldehydes, ketones and even acid chlorides without affecting any other reducible groups, but it has no action upon carboxylic acid or esters. Consequently this reagent is employed for reducing various types of compounds, namely, aldonic lactones (Wolform and Wood, *ibid.*, 1951, **73**, 2993; Abdel-Akher, Hamilton and Smith, *ibid.*, p. 4691), esters and sodium salts of acids of sugar (Wolform and Anno, *ibid.*, 1952, **74**, 5583), aldehydo cardiac glycosides or aglycones (Hunger and Reichstein, *Chem. Ber.*, 1952, **85**, 635) and keto-steroids * (Elisberg, Vanderhaeghe and Gallagher, *J. Amer. Chem. Soc.*, 1952, **74**, 2814). Fission of glycosidic linkage also takes place (Hough, Jones and Richards, *Chem. Ind.*, 1953, 1064) if the compound is subjected to a prolonged treatment with sodium borohydride. Although the use of sodium borohydride in the reduction of various homocyclic compounds has already been reported, very little work appears to have been made on the application of this reagent in heterocyclic systems (cf. Whaley and Robinson, *J. Amer. Chem. Soc.*, 1953, **75**, 2008; Witkop *et al.*, *ibid.*, 1953, **75**, 3361, 4474; Woodward *et al.*, *ibid.*, 1954, **76**, 4749).

The present work has been undertaken with a view to investigating its reducing action on carbinolamine bases** belonging to heterocyclic series, e.g., berberine, cotarnine and hydrastinine. Upon treatment with sodium borohydride in methanol or ethanol at ordinary temperature, berberine and the other two bases undergo facile reduction, furnishing dihydro-anhydro derivatives. In case of berberine, the reduction product can be readily isolated, but with other two, the reduction products are obtained only as an oil. The oily mass has been subsequently converted into well crystalline salts. The reduction products (Table I) lack the properties of carbinolamine as they do not form any oxime or produce salts without loss of water.

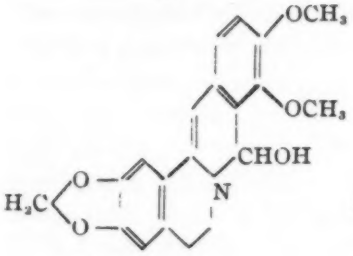
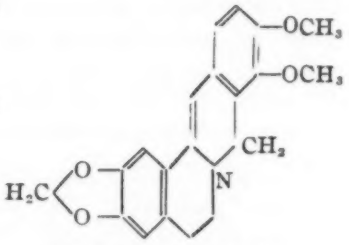
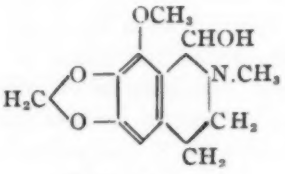
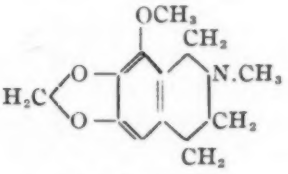
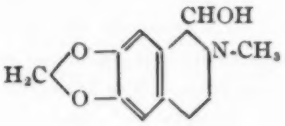
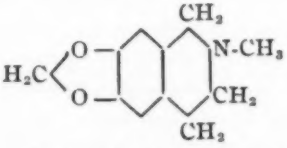
Berberine, cotarnine and hydrastinine have also been reduced with $LiAlH_4$, furnishing the identical dihydro-anhydro derivatives produced by sodium borohydride reduction of

* It is found that in steroids 3 keto group is reduced much more readily than that at C_{17} or C_{20} with sodium borohydride.

** This study was necessitated during our work on the constitution of Rauwolfinine (Bose, this *Journal*, 1954, **31**, 47, 311, 691) and ajmaline (Chatterjee and Bose, *ibid.*, p. 17, *Science & Culture*, 1955, **20**, 606).

the corresponding bases. This is therefore a new observation made by the present author that sodium borohydride runs parallel with lithium aluminium hydride in reducing Schiff's bases. Further, sodium borohydride appears to be a very useful reagent for the detection of carbinolamine group (-N-CHOH) in het rocyclic compounds and is much better than $LiAlH_4$ as the operations involved (in cases of sodium borohydride) are much simpler.

TABLE I

Compound.	Reduction product.	M.P. of reduction product.
 Berberine.	 Dihydro-anhydroberberine.	166-67°
 Cotarnine.	 Hydrocotarnine (isolated as hydrobromide).	† Hydrobromide, 227-28°
 Hydrastinine.	 Hydrohydrastinine (isolated as picrate and hydrobromide)	Picrate, 173-74° Hydrobromide, 271° (decomp.)

Formation of dihydro-anhydro compounds from the corresponding carbinolamine bases can readily be recognised from their I.R. spectra. The I.R. spectra* of berberine, cotarnine and hydrastinine exhibit bands at 3.0 μ region (Table II) which are solely due to carbinolamine hydroxyl.

† Witkop (*J. Amer. Chem. Soc.*, 1953, **75**, 4474) reported the m.p. 229-30°.

* The distinct absence of —C = N band at 6 – 6.05 μ in the I.R. spectra of berberine, cotarnine and hydrastinine confirms that under ordinary conditions the carbinolamine structure is the best representative of the above three bases.

TABLE II

Compounds.	Phase.	Bands at 2.5–3μ.
Berberine	Mineral oil	2.84 μ
Dihydro-anhydroberberine	Nujol	Nil
Cotarnine	$CHCl_3$	2.71, 2.79 μ
Hydrocotarnine hydrobromide	Nujol	Nil
Hydrastinine	$CHCl_3$	2.77, 2.82 μ
Hydrohydrastinine hydrobromide	Nujol	Nil

These bands totally disappear in the I.R. spectra of the reduction products which are exactly as expected if the carbinolamine bases are reduced to dihydro-anhydro derivatives. Thus, the course of reduction is easily settled through the study of infra-reds pectrum.

EXPERIMENTAL

Reduction of Berberine

With Sodium Borohydride.—To berberine (0.18 g.), dissolved in 95% alcohol (20 c.c.), sodium borohydride (50 mg.) was added. The yellow colour of the solution at once disappeared with a brisk evolution of hydrogen. The whole mixture was kept in a frigidaire for 48 hours when needle-spaped crystals were deposited. It was then diluted with water (30 c.c.), and filtered. The crystals, thus obtained, were repeatedly washed with water, dried and twice crystallised from methanol when fine clusters of needles were obtained, m.p. 166-67°, yield 70 mg. The product was found to be identical with dihydro-anhydroberberine *, the mixed m.p. determination of which with an authentic sample did not show any depression. (Found in a dry sample : C, 71.38; H, 5.52; N, 4.09. Calc. for $C_{20}H_{19}O_4N$: C, 71.19; H, 5.68; N, 4.15 per cent).

With $LiAlH_4$.—To a cold solution of berberine (0.1 g.) in dry chloroform (100 c.c.) a slurry of $LiAlH_4$ (20.0 mg.) in dry chloroform (10 c.c.) was added, kept at room temperature for 2 hours and then refluxed on a steam-bath for 4 hours. The mixture was cooled in ice, and water (4 c.c.) was added to decompose the excess of $LiAlH_4$. It was then filtered and the filtrate was evaporated to dryness under reduced pressure. The residue left was dried and redissolved in chloroform. The hot solution was then filtered and the clear filtrate was again evaporated to dryness and the residue, thus left, was crystallised from methanol when needle-shaped crystals were obtained, m.p. 166-67°, yield 50 mg. The compound was found to be identical with dihydro-anhydroberberine, obtained from sodium borohydride reduction of berberine.

Reduction of Cotarnine

With Sodium Borohydride.—To a cold yellow solution of cotarnine (0.3 g.) in absolute methanol (10 c.c.) sodium borohydride (0.2 g.) was added. It rapidly dissolved with the evolution of hydrogen and the yellow colour of the solution disappeared. The mixture was kept as such in the frigidaire for two days and then concentrated to a

* Gadamer (*Arch. Pharm.*, 1910, **248**, 670) and Perkin (*J. Chem. Soc.*, 1918, **113** 722) reported the m.p. of the compound as 164-66° and 168-70° respectively.

small volume and poured into water (100 c.c.). The aqueous solution was basified with NaOH and extracted four times with ether. The total ether extract (200 c.c.) was washed with water and dried; on being freed from the solvent it left an oil which did not crystallise from any solvent. The oil did not solidify even after chromatography over alumina. It was next dissolved in absolute alcohol and to that solution a few drops of 48% aqueous hydrobromic acid was added when crystals of the hydrobromide separated out. It was sparingly soluble in alcohol and it was purified by three crystallisations from absolute alcohol, m.p. 227-28°, yield 180 mg. The substance was found identical with an authentic sample of hydrocotarnine hydrobromide. Wright (*J. Chem. Soc.*, 1877, **32**, 525) records m.p. 236-37°. (Found: in a dried sample: C, 44.54; H, 5.23; N, 4.57; Br, 26.31. Calc. for $C_{12}H_{15}O_3N$, HBr: C,44.37; H, 5.3; N, 4.63; Br, 26.16 per cent).

With $LiAlH_4$.—To a cold slurry of $LiAlH_4$ (0.1 g.) in dry chloroform (10 c.c.) was slowly added a solution of cotarnine (0.5 g.) in 30 c.c. of dry chloroform. During the addition vigorous reaction took place and the deep red colour of the solution disappeared. The mixture was left as such for 2 hours and then refluxed on the water-bath for 4 hours. It was cooled in ice and decomposed by water (5 c.c.) and filtered. The filtrate was shaken with 2*N*-HCl (30 c.c.). The acid solution was cooled, basified with NaOH and extracted with ether. The combined ether extract (200 c.c.) was washed with water, dried and then concentrated when an oil was left. This was dissolved in absolute alcohol and converted into hydrobromide by adding 48% aqueous hydrobromic acid. The hydrobromide on twice crystallisation from absolute alcohol melted at 226-27°, yield 210 mg. It was found identical with that obtained from cotarnine by reduction with sodium borohydride.

Reduction of Hydrastinine

With Sodium Borohydride.—To a solution of hydrastinine (0.5 g.) in dry methanol was added sodium borohydride (0.3 g.) in the cold. A vigorous reaction took place with the disappearance of the yellow colour of the solution. The mixture was kept for 40 hours and worked up in the usual way as in the case of cotarnine. Removal of the ether yielded an oil which did not crystallise from any solvent. The oil did not solidify even after chromatography over alumina. It was then dissolved in absolute alcohol and converted into the hydrobromide by adding few drops of 48% aqueous hydrobromic acid. The crude hydrobromide was purified by twice crystallisation from absolute alcohol, m.p. 271-72° (decomp.), yield 300 mg. This hydrobromide was found identical in all respects with an authentic sample of hydrohydrastinine hydrobromide *. (Found in a dried sample: C, 48.62; H, 5.14; N, 5.22; Br, 29.62. Calc. for $C_{11}H_{13}O_2N$, HBr: C, 48.53; H, 5.15; N, 5.15; Br, 29 41 per cent).

Hydrohydrastinine Pictrate.—To a solution of hydrohydrastinine hydrobromide (20 mg.) in water was added an aqueous solution of picric acid. A yellow precipitate was obtained which was filtered and made free from picric acid by repeatedly washing with water. The dry crude picrate was then crystallised twice from rectified spirit

* Pyman and Remfry (*J. Chem. Soc*, 1912, **101**, 1595) record m p. 293°.

when yellow shining flakes of hydrohydrastinine picrate was obtained, m.p. 173-74°, yield 10 mg. [Found in a dried sample: N, 11.24. $C_{11}H_{13}O_2N$, $C_6H_2(OH)(NO_2)_3$ requires N, 11.18 per cent].

With $LiAlH_4$.—Hydrastinine (0.5 g.) was reduced with $LiAlH_4$ (0.1 g.) in exactly the same manner as in the case of cotarnine. Working up of the reaction product produced an oil which was successfully converted into well crystalline hydrobromide, m.p. 271-72°, and picrate, m.p. 173-74°. Both the hydrobromide and pictrate were found to be identical with those obtained from hydrastinine by sodium borohydride reduction.

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COMPONENT FATTY ACIDS AND UNSAPONIFIABLES IN SHARK LIVER OIL

By G. G. Kamath and N. G. Magar

Waghbeer and Khada mushi liver oils were studied for their component fatty acids by low temperature separations, methyl ester fractionation and alkali isomerisation. The nature of the two oils studied is different: in Waghbeer liver oil, C_{20} and C_{22} acids predominate over the C_{18} and C_{16} acids, whereas in Khada mushi liver oil, C_{18} acids constitute the major portion. The unsaponifiables of the two oils were studied chromatographically and spectrophotometrically. Cholesterol and vitamin-A are present in both these samples. Presence of kitol is also confirmed.

Kamath and Magar (this *Journal*, 1953, **30**, 335) observed that Waghbeer liver oil (*Galeocerdo tigrinus*) with a comparatively low vitamin-A potency was more stable than the high-potency liver oil of Khada mushi (*Carcharinus melanopterus*). An ultraviolet absorption study by the authors (*Ind. J. Med. Res.*, 1953, **41**, 339) revealed a difference in the characteristics of these oils. An attempt has been made in the present work to throw more light on these observations by studying the component fatty acids and the unsaponifiables of these oils.

Experimental

Fresh samples of livers from the identified species were digested in an autoclave for 15 minutes at 15 lbs. pressure p. s. i. with one-third its weight of water. The livers were very rich in oil and yielded 50-60% oil. This was separated and dried over anhydrous Na_2SO_4.

The unsaponifiable matter and the mixed fatty acids were obtained by a method developed by Hilditch ("Chemical Constitution of Natural Fats", 1947, p. 465).

Analysis of Fatty Acids.—The fatty acids were primarily resolved into different groups using the low temperature scheme of Gupta and Hilditch (*Biochem. J.*, 1951, **48**, 137).

Linoleic and linolenic acids were estimated in the unsaturated groups as recommended by Hilditch, Morton and Riley (*Analyst*, 1945, **70**, 68). Other polyunsaturated acids were determined by the method suggested by Herb and Riemenschneider (*Anal. Chem.*, 1953, **25**, 953). The absorption spectra of the alkali-isomerised samples were also studied using a Beckman spectrophotometer (Model DU).

The methyl esters of the fatty acids were distilled under vacuum, using E. H. P. column, designed by Longenecker (*J. Soc. Chem. Ind.*, 1937, **56**, 199T). Saponification equivalent (S. E.) and iodine value (I. V.) were determined by the A. O. C. S. official methods (1951) and the calculations were based on the recommendations of Hilditch (*loc. cit.*, p. 484).

Analysis of Unsaponifiable Matter.—About 0.3 g. of unsaponifiable matter was chromatographed on a 10 cm. column of alumina according to Swain's method (*J. Fish Res.*

Bd. Canada, 1948, **6**, 7). The absorption spectra of the fractions obtained were studied in the ultraviolet using ethyl alcohol as a solvent.

Carr-Price reagent was used for the detection of vitamin-A, dry HCl gas for squalene, and Libermann-Burchard test for cholesterol. Vitamin-A was estimated spectrophotometrically ("Methods of Vitamin Assay", 1951, p. 36) and cholesterol colorimetrically.

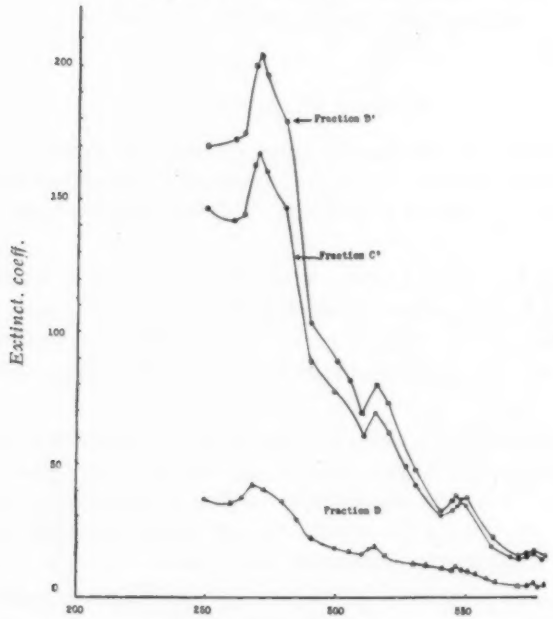
Waghbeer Liver Oil

The oil (165 g., S. E. 385.3; I. V. 66.9) gave 131.7 g. of fatty acids (S. E. 301.1 ; I. V. 65.3) and 28.0 g. of unsaponifiable matter. Mixed fatty acids (123.8 g.) were subjected to the low temperature crystallisation, using 10% w/v solutions. The four groups of fatty acids obtained are shown in Table I.

The methyl ester fractionation data for groups A, B and C are presented in Table II. The alkali isomerisation data for group D are shown in Table III, and the absorption spectra after alkali isomerisation are shown in Fig. 1.

FIG. 1

Abs. spectra after alkali- isomerisation.



(7.5 g. KOH-glycol : 170°-15 min EtOH).

From the data in Tables I-III, the component acids present in groups A, B, C and D were calculated, and hence the composition of the mixed fatty acids in the whole oil (Table IV).

TABLE I

Separation of acids of Waghbeer liver oil by low temperature.

Group.	Description.		Weight.		I. V	S. E
A	−10°	Ether insoluble	13.0 g.	10.50%	10.5	279 6
B	−10°	Ether soluble				
	−30°	Ether insoluble	30.5	24 63	22.2	272.5
C	−30°	Ether soluble				
	−55°	Acetone insoluble	42.5	34.34	76.6	285.1
D	−55°	Acetone soluble	37.8	30.53	109.2	321.0

TABLE II

Fractionation of methyl esters of A, B and C acids from Waghbeer liver oil.

Methyl esters of A acids.				Methyl esters of B acids.				Methyl esters of C acids.			
No.	Wt.	S.E.	I.V.	No.	Wt.	S.E	I.V.	No.	Wt.	S.E.	I.V.
A_1	2 384 g.	260.1	3.77	B_1	3.465 g.	268 3	8.30	C_1	4.912 g.	269.5	42.30
A_2	2.356	271.3	3.66	B_2	3.514	268.9	7.24	C_2	3.451	273.5	43.58
A_3	1.851	276.8	4.28	B_3	3 055	271.0	6.71	C_3	3 102	284.3	49.85
A_4	5.214	326.0	19,0	B_4	3.603	272.1	10.33	C_4	3.539	289 4	71.63
				B_5	3 828	278 6	24 66	C_5	3.550	295.7	74.27
				B_6	2.667	301.0	34.44	C_6	3.264	297.7	75.83
				B_7	7.428	* 322.0	* 40.40	C_7	2.173	327.9	110.8
								C_8	8.922	* 337.7	* 99.8
	11.80				27.560				32.913		

* Values for esters, freed from unsaponifiables.

TABLE III

Alkali-isomerisation data for unsaturated groups of fatty acids.

	Condition of isomerisation.	Group.	% Linoleic.	% Linolenic.	% Archidonic.	% Clupanodonic.	% Hexaenoic
1	7.5 g KOH-glycol	D	—	7.92	Present.	Present.	Present.
	170° for 15 min.	C′	—	31.43	,,	,,	,,
	(Ethanol)	D′	—	38.50	,,	,,	,,
2	7.5 g. KOH-glycol	D	1.34	—	—	—	—
	180° for 60 min.	C′	Nil	—	—	—	—
	(Ethanol).	D′	Nil	—	—	—	—
3.	21% KOH-glycol	D	—	—	1.48	1.13*	Traces
	180° for 15 min	C′	—	—	5.95	6.93**	,,
	(Methanol)	D′	—	—	7.64	8 46**	0.5?

* Calculated as C_{22} acids.

** Calculated as 50% C_{20} + 50% C_{22} acids.

TABLE IV

Component acids in Waghbeer liver oil.

Acids.	Weight percentage in groups. A.	B.	C.	D.	Total. Wt.%	Mol.%.
Myristic	0.67	0.25	...	...	0 92	1.17
Palmitic	4.43	12.11	5.00	...	21.54	24.49
Stearic	0 52	3.18	2.61	...	6.31	6.47
Arachidic	3.51	2.71	0.17	...	6.39	5.96
Unsaturated:						
C_{14} (−2H)	0.02	...	...	...	0.02	0.03
C_{16} (−2H)	0.16	1.61	5.31	...	7.08	8.11
C_{18} (−2H)	0.06	1.16	9.67	...	10.89	11.24
(−4H)	...	—	...	0.41	0.41	0.43
(−6H)	...	...	...	2.42	2.42	2.53
C_{20} (−2H)	1.13	3.61	6.45	8.07	19 26	18.07
(−8H)	...	...	1.25	0.45	1.70	1.63
C_{22} (−2H)	...	...	3.88	18.84	22.72	19.57
(−10H)	...	...	...	0 34	0.34	0.30
C_{24} (−12H)	...	...	...	Traces	Traces	Traces
Total	10.50	24 63	34.34	30.53	100	100

TABLE V

Separation of acids of Khada mushi liver oil by low temperature.

Group.	Description.	Weight.		I.V.	S.E.
A′	−30° Ether insoluble	45.0 g.	34.48%	54.75	260.0
B′	−30° Ether soluble;				
	−50° Acetone insoluble	35.0	26 82	103.1	264.7
C′	−50° Acetone soluble	23 0	17 63	185 8	278.5
	−70° acetone insoluble.				
D′	−70° acetone soluble	27.5	21.07	209.0	280.2

TABLE VI

Fractionation of methyl esters of groups A′ and B′ acids from Khada mushi liver oil.

	Methyl esters of A′ acids.				Methyl esters of B′ acids.		
No.	Wt.	S E.	I.V.	No.	Wt.	S.E.	I.V.
A_1	2.593 g.	246.9	12.80	B_1	2.535 g.	244.9	29.78
A_2	2 853	261.6	19 10	B_2	2.613	262.8	33 71
A_3	2.795	261.1	19.45	B_3	3 123	268.2	37.55
A_4	2 972	265.4	21.29	B_4	2.727	273.0	51.10
A_5	2.887	267.6	22.20	B_5	3 232	283.1	76.83
A_6	2.956	268 1	23 30	B_6	2.993	289.4	87.86
A_7	2 994	272.6	33 48	B_7	3.321	294.1	166.0
A_8	2.776	286.4	39.69	B_8	4.673	*299.0	*201.6
A_9	3.352	288 9	44.96				
A_{10}	2.853	289.4	60.42				
A_{11}	6.099	*291.5	*139.3				
	35.130				25 217		

* Values for esters freed from unsaponifiables.

Khada Mushi Liver Oil

The oil (148 g., S. E. 267.5, I. V. 129.5) gave 2.76 g. of unsaponifiable matter and 138.0 g. of mixed fatty acids (S. E. 267.2; I. V. 128.9). The results of low-temperature separation with 130.5 g. of mixed fatty acids are shown in Table V. The other relevant data are incorporated in Tables III, VI and VII, and in Fig. 1.

Unsaponifiable Matter

The details of the two oils studied for unsaponifiable matter are shown below.

Oil.	S. E.	I. V.	Non-sap. matter.
Waghbeer liver oil	352.6	70.75	11.16 %
Khada mushi liver oil	310.1	93.90	4.59

The results of Swains chromatography are presented in Table VIII and the absorption spectra of the fractions in U. V. are shown in Figs. 2 and 3.

TABLE VII

Component acids in Khada mushi liver oil.

	Weight percentage of groups.				Total	
Acids.	A'.	B'.	C'.	D'.	Wt. %	Mol. %
Myristic	3.90	2.25	...	...	6.15	7.24
Palmitic	11.97	4.89	...	...	16.86	17.70
Stearic	3.32	0.39	...	...	3.71	3.51
Arachidic	...	1.13	...	...	1.13	0.97
Unsaturated:						
C_{14} (−2H)	0.49	0.79	...	...	1.28	1.52
C_{16} (−2H)	5.19	5.57	3.27	3.15	17.18	18.17
C_{18} (−2H)	5.89	4.67	6.55	6.31	23.42	22.30
(−4H)	3.72	3.29	...	...	7.01	6.72
(−6H)	...	3.84	5.54	8.12	17.50	16.90
C_{20} (−8H)	...	...	1.05	1.61	2.66	2.35
(−10H)	...	...	0.61	0.89	1.50	1.33
C_{22} (−10H)	...	...	0.61	0.89	1.50	1.22
(−12H)	...	...	Traces	0.10 (?)	0.10 (?)	0.08 (?)
Total	34.48	26.82	17.63	21.07	100	100

TABLE VIII

Chromatographic separation of the unsaponifiables in liver oils.

		Waghbeer			Khada mushi.		
Eluent.	Fraction.	Wt.	Vit A (I.U./g.)	Cholesterol.	Wt.	Vit A. (I.U./g.).	Cholesterol.
Petroleum ether (200 ml.)	1	38.5 %	25200	...	16.6 %	31,5500	...
CCl_4 (100 ml.)	2	19.4	...	7.0%	30.0	...	20 4 %
Ethyl ether (100 ml.)	3	38.9	...	...	43.3	...	...
EtOH (75 ml.)	4	2.0	...	...	6.7	..	...

Discussion

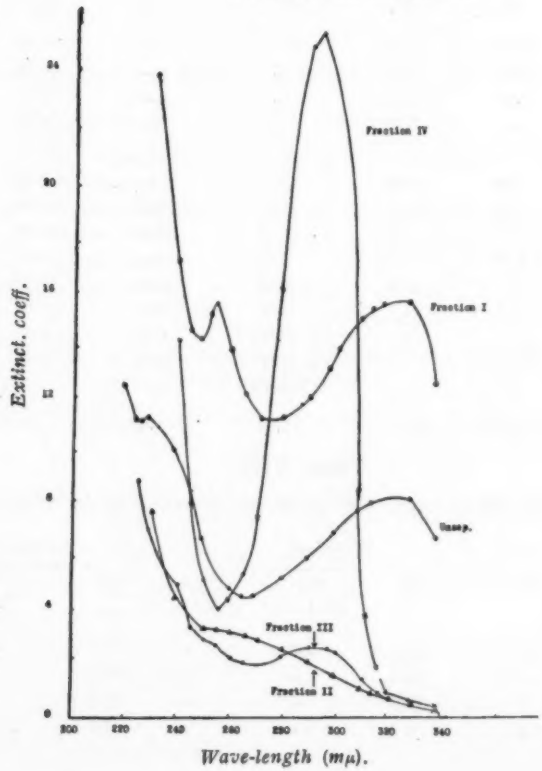
Component Fatty Acids

The Waghbeer liver oil contains 35.16% saturated acids, palmitic acid being predominant, viz., 21.54%. Stearic and arachidic acids are present in the same proportions, 6.31% and 6.39%. The unsaturated acids amounting to 64.84% comprise a wide variety of acids. C_{20} and C_{22} acids, 20.96% and 23.06% respectively, predominate over the C_{16} and C_{18} acids (7.08% and 13.72% respectively). The mean unsaturation of all these acids is only slightly more than monoethenoid series. This was expected from the low iodine value of the oil and its vitamin-A stability. It is obvious that the biohydrogenation (cf. Lovern, *Biochem. J.*, 1936, **30**, 2023) of the various fatty acids in the liver has proceeded till one double bond remains to be saturated.

Khada mushi liver oil differs from the Waghbeer liver oil, and contains 27.85% saturated and 72.15% unsaturated acids. Palmitic acid (16.86%) is the major component amongst the saturated acids. This is followed by myristic acid (6.15 %). Stearic and arachidic acids are present in small amounts. C_{18} acids, comprising 47.93%,

FIG, 2

Waghbeer liver oil (unsap.).



predominate the unsaturated acids. Next comes palmitoleic acid ; C_{20} and C_{22} acids are once again present in small amounts.

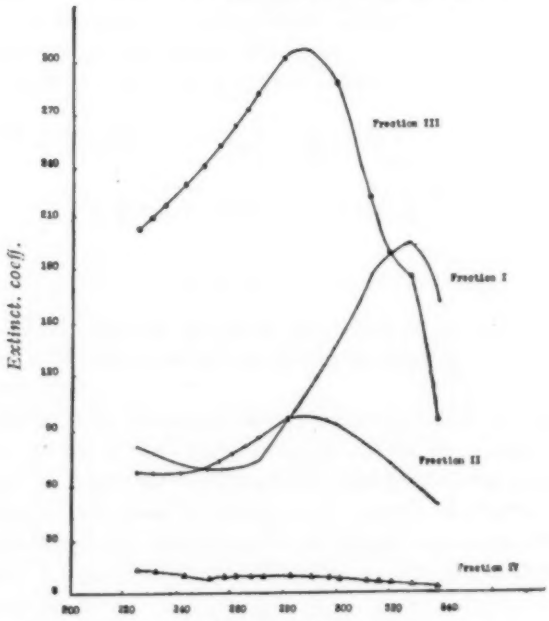
It could thus be observed that whereas C_{20} and C_{22} acids with lesser unsaturation predominate in Waghbeer, highly unsaturated C_{18} and C_{16} acids, especially C_{18} acids, dominate the Khada mushi liver oil. This also explains the large difference in the S. E. of the two oils studied.

It is a matter of interest to note that in both the oils linolenic acid is about 2·5 times of linoleic acid. Lovern (*Biochem. J.*, 1932, **26**, 1976) has suggested that linoleic acid is not essential for the metabolism of Halibut, and is therefore destroyed in its body. A similar explanation is not improbable in Elasmobranch oils to which the oils analysed belong.

The absorption spectra of the unsaturated groups of acids after alkali-isomerisation reveal the presence of different polyunsaturated acids, including hexaenoic acid (Fig. 1).

FIG. 3

Khada mushi liver oil (unsap.).



Unsaponifiables

The U. V. absorption spectra reveal the presence of vitamin-A concentrates in the petroleum ether-eluted fractions in both the oils. No squalene was detected in these fractions. Cholesterol was absent.

The CCl_4 - eluted fractions were rich in cholesterol. This is also seen from their spectra which show maxima at 265-270 mμ.

The fractions eluted by ethyl ether were unsaturated in nature ; they decolorised bromine water readily and developed a red Carr-Price reaction, characteristic of kitol.

The alcohol-eluted fraction in Waghbeer liver oil was similar to ethyl ether-eluted fraction. In Khada mushi liver oil, this fraction did not show any substance of interest and gave a flat curve.

It can thus be seen that the major constituents of the unsaponifiables from both the oils are vitamin-A and cholesterol. The presence of kitol is also confirmed by this study.

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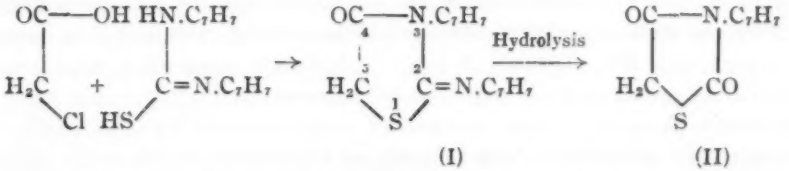
STUDIES ON 3-*o*-TOLYL-2 : 4-THIAZOLIDIONE

By Prithwi Nath Bhargava and Ravindra Pratap Rao

3-*o*-Tolyl-2 : 4 thiazolidione has been synthesised by condensing *S*-di-*o*-tolylthiourea with monochloroacetic acid in glacial acetic acid, and its constitution established.

Dains, Irvin and Harrel (*J. Amer. Chem. Soc.*, 1921, **43**, 613) prepared a few 3-aryl-2-arylimino-4-thiazolidones. By the hydrolysis of these thiazolidones they obtained 3-aryl-2 : 4-thiazolidiones. Klare, Markley and Reid (*ibid.*, 1930, **52**, 2137) further studied the secondary formation of 3-phenyl-2 : 4-thiazolidione along with the primary formation of 3-phenyl-2-phenylimino-4-thiazolidone, when *S*-diphenylthiourea was treated with monochloroacetic acid in alcoholic medium. This reaction has now been extended to the synthesis of 3-*o*-tolyl-2 : 4-thiazolidione, not described in the literature as yet, by the condensation of *S*-di-*o*-tolylthiourea with monochloroacetic acid in the presence of glacial acetic acid. During studies on the effect of reaction conditions on the preparation of 3-*o*-tolyl-2 : 4-thiazolidione, the highest yield (99.28%) is reported when 6 c.c. of glacial acetic acid per 1.28 g. of *S*-di-*o*-tolylthiourea is employed and the time of reflux for 3½ hours is maintained. On increasing the time of reflux to more than 5½ hours, the product is found to resinify, probably due to decomposition.

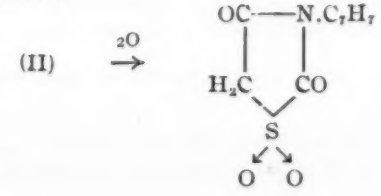
The structure of 3-*o*-tolyl-2 : 4-thiazolidione has been confirmed by the synthesis of 3-*o*-tolyl-2 *o*-tolylimino-4-thiazolidone (Bhargava *et al.*, this *Journal*, 1955, **32**, 50) and its subsequent hydrolysis to 3-*o*-tolyl-2 : 4-thiazolidione, as illustrated by the following reactions:



(I) (II)

The compound (II) obtained in a white crystalline form (m.p. 154°) remained unchanged with cold or hot dilute potassium hydroxide solution. On fusion with sodalime, *o*-toluidine was obtained.

On mercuration with mercuric acetate, 3 acetoxymercuri-*o*-tolyl-2 : 4-thiazolidione is obtained. The acetoxymercuri group probably enters the phenyl nucleus as usual. The thiazolidione is found to condense with vanillin yielding 3-*o*-tolyl-5-vanillal-2 : 4-thiazolidione, thereby indicating the presence of a reactive methylene group (-CO-CH_2S). Further, on oxidation with chromic acid in glacial acetic acid (Shriner, Struck and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060), 3-*o*-tolyl-2 : 4-thiazolidione sulphone (m.p. 85°) has been obtained.



EXPERIMENTAL

3-o-*Tolyi*-2 : 4-*thiazolidion*$_e$ (II).—*S*-Di-*o*-tolylthiourea (1.28 g.), varied quantities of monochloroacetic acid (0.958-1.0 g.) and glacial acetic acid (5-12.5 c.c.), a little more than the molar quantity required, were refluxed on a water-bath in a round bottomed flask. After condensation the compound separated in a crystalline acicular form on cooling. Excess of water was added and the precipitate filtered on a Büchner funnel. After washing with water to remove the acid and filtration, the precipitate was dried and crystallised from absolute alcohol in a white crystalline form, m.p. 154°, yield (max.) 99.28%. On increasing the time of reflux to more than 5½ hours. the product resinified due to gradual decomposition. (Found : S, 15.42. $C_{10}H_9O_2NS$ requires S, 15.46 per cent).

3-*Acetoxymercuri*-o-*tolyl*-2 : 4-*thiazolidione*.—The preceding compound (II, 1 g.) was dissolved in glacial acetic acid (20 c.c.) and to this absolute alcohol (15 c.c.) and mercuric acetate (1.56 g.), dissolved in water (15 c.c.) and acidified with acetic acid, were added. On keeping overnight, a precipitate was obtained, which was filtered, washed respectively with hot water, alcohol and dilute acetic acid, dried and crystallised from absolute alcohol in a white crystalline form, m.p. 168°. (Found : Hg, 42.62. $C_{12}H_{11}O_4NSHg$ requires Hg, 43.08 per cent).

3-o-*Tolyl*-5-*vanilial*-2 : 4-*thiazolidione*.—A mixture of vanillin (3 g.), compound (II) (2 g.), piperidine (2 c.c.) and dry benzene (15 c.c.) was refluxed on a water-bath for 3 hours and then freed from benzene. The product was treated with cold absolute alcohol, in which the product dissolved and unchanged thiazolidione remained insoluble. After filtration, the alcohol was distilled off and the product crystallised from benzene in a yellow form, m.p. 66°. (Found : S, 9.51. $C_{18}H_{15}O_4NS$ requires S, 9.38 per cent).

3-o-*Tolyl*-2 : 4-*thiazolidione Sulphone*.—Compound (II) (2.5 g.) was dissolved in glacial acetic acid (15 c.c.), taken in a 100 c.c. round bottomed flask, and treated slowly with chromic acid anhydride. After refluxing on a water-bath for about 20 minutes, a precipitate was obtained. It was filtered, washed with ice water, dried and crystallised from absolute alcohol in a pale yellow form, m.p. 85° (decomp.). (Found : S, 13.64. $C_{10}H_9O_4NS$ requires S, 13.34 per cent).

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CONDENSATION OF ARYL DIAZONIUM SALTS WITH REACTIVE UNSATURATED COMPOUNDS. PART VII*. ACTION OF ARYLDIAZONIUM CHLORIDES WITH β-BENZOYLACRYLIC ACID

By Hari Shanker Mehra and Kunj Behari Lal Mathur

Aryldiazonium chlorides yield chalkones when interacted with *cis*- and *trans*-β-benzoylacrylic acids under Meerwein's conditions. The aryl radical attacks the carbon atom α to COOH group, and this initial coupling is followed by decarboxylation. The chalkones have been recovered from the complex reaction mixture by extraction with aqueous potassium bisulphite or H_2SO_4 (80-85%).

β-Benzoylacrylic acid has not so far been subjected to any homolytic addition reaction. Because of the non-identity of the two activating groups, -CO- and -COOH, in union with the olefinic linkage in the acid

$$C_6H_5CO-\overset{\beta}{C}H=\!=\!=\overset{\alpha}{C}H-COOH$$
(I)

addition of a radical may occur at the α or β carbon atom. Mathur and co-workers (this *Journal*, 1947, **24**, 123; 1951, **28**, 540) have utilised Meerwein's diazo reaction (Meerwein *et al.*, *J. parkt. Chem.*, 1939, *ii*, **152**, 251) to decide the orientation of free radicals in monosubstituted maleic acids (II, R= Me or Br). It was found in these cases that decarboxylation occurred during the coupling reaction and α-methyl- or α-bromocinnamic acids were produced:

$$\underset{\beta}{HO_2C-CH}=\!=\!=\underset{\alpha}{C}(R)-CO_2H + ArN_2Cl = Ar\underset{\beta}{CH}=\!=\!=\underset{\alpha}{C}(R).COOH + CO_2 + N_2 + HCl \quad \ldots (1)$$
(II) (III)

The formation of the cinnamic acids (III, R= Me or Br) showed that the aryl radical went to the β-carbon atom of the acids (II). The reaction has now been extended to *cis*- and *trans*-β-benzoylacrylic acids (I) to see how a free radical will add to these acids.

When *p*-chlorobenzenediazonium chloride is coupled with *trans*-β-benzoylacrylic acid in the presence of sodium acetate and cupric chloride, the onset of the reaction is marked by effervescense which is over in about three hours. The gas evolved during the reaction contains substantial amount of carbon dioxide, suggesting the occurrence of decarboxylation which may have been brought about as a result of a change, e.g.,

$$C_6H_5COCH=\!=\!=CH.COOH + ClC_6H_4N_2Cl = C_6H_5.CO.CH=\!=\!=CH.C_6H_4Cl + N_2 + HCl + CO_2 \quad \ldots (2)$$

* The paper 'Coupling of aconitic acid and itaconic acid with certain diazonium chlorides' (*J. Amer. Chem. Soc.*, 1953, **75**, 3240) may be considered as Part VI of this series.

No acidic coupling product seems to be present in the reaction mixture. But owing to the presence in it of a tarry matter, recovery of the expected *p*-chlorochalkone with the help of solvents has not been possible. It has, however, been found practicable to recover this chalkone by extraction with boiling aqueous potassium bisulphite, followed by basification with strong alkali in the cold (cf. Knoevenagel and Morrisse, *Ber.*, 1904, **27**, 4049; also Kratzl and Daubner, *Ber.*, 1944, **77B**, 519):

$$C_6H_5.CO.CH{=}CH.C_6H_4Cl \underset{NaOH}{\overset{KHSO_3}{\rightleftharpoons}} C_6H_5CO.CH_2.\underset{SO_3K}{CH}.C_6H_4Cl \qquad \ldots \quad (3)$$

The isolation of *p*-chlorochalkone conforms to the occurrence of the coupling reaction as formulated in reaction (2).

Ortho- and *m*-chlorobenzene-*p*-bromobenzene-,*o*-,*m*- and *p*-nitrobenzene-diazonium chlorides have also been coupled with *β*-benzoylacrylic acid. In every case, the evolved gas contains carbon dioxide and the appropriate chalkone has been isolated. In experiments with halogenated diazonium chlorides, the recovery of the chalkone has been possible by extraction with potassium bisulphite. But because of side reactions, this reagent is not found suitable for extraction of the nitrochalkones, supposed to be formed from interaction of nitrobenzenediazonium chlorides with *β*-benzoylacrylic acid. The nitrochalkones have been extracted with 80-85% sulphuric acid, followed by dilution of the acid extract with ice-water (vide Vorländer and Mumme, *Ber.*, 1903, **36**, 1479). For the halogenated chalkones, this mode of extraction appears to be less satisfactory. The *p*-substituted diazonium chlorides afford fair yields of the chalkone (19-27%). Yields are poor (*ca.* 4%) with *o*- and *m*-chlorobenzenediazonium chlorides.

Diazonium salts couple with *cis-β* benzoylacrylic acid comparatively readily. The evolved gases contain carbon dioxide, indicating that in this case also the coupling process results in the formation of the chalkones. Utilising the potassium bisulphite or sulphuric acid extraction, the chalkones have been recovered in yields more or less similar to those obtained from *trans*-benzoylacrylic acid.

The main reaction of aryldiazonium chlorides with *cis-* and *trans-β*-benzyolacrylic acid thus is as shown below:

$$\underset{\substack{\beta \quad \alpha \\ \beta\text{-Benzoylacrylic acid.}}}{C_6H_5.CO.CH{=}CH.COOH} + ArN_2Cl = \underset{\substack{\beta \quad \alpha \\ \text{Chalkone.}}}{C_6H_5CO.CH{=}CH.Ar} + CO_2 + N_2 + HCl \quad (4).$$

In this connection it is necessary to postulate (cf. Koelsch and Boekelheide, *J. Amer. Chem. Soc.*, 1944, **66**, 412) the formation in the initial stage of an intermediate free radical (e.g., IV or V):

$$C_6H_5CO.\underset{\substack{| \\ Ar \\ (IV)}}{CH}-CH-COOH \xleftarrow{Ar.} C_6H_5CO.CH{=}CH.COOH \xrightarrow{Ar.} C_6H_5COCH-\underset{\substack{| \\ Ar \\ (V)}}{CH}.COOH$$

The formation of chalkones (Reac. 4) indicates that the radical (IV) is formed in preference to (V). This may be explained by considering that the lone electron in (IV) will have a better scope for resonance stabilisation in the reactive -CO group than in the COOH group of (V). Further, the easy elimination of carbon dioxide culminating in the formation of the chalkone can be explained by supposing the formation of a carbonium cation (Koelsch *et. al., loc. cit.*; Mathur *et al., loc. cit.*; Johnson and Heinz, *J. Amer. Chem. Soc.*, 1949, **71** 2916).

It is incidentally also clear that the aryl radical in the Meerwein diazo reaction with β-benzoylacrylic acid (I) attaches itself to its α-carbon atom. Considering that hydrochloric acid addition to this acid results in the formation of α-chloro-β-benzoylpropionic acid (Bougault, *Ann. chim.*, 1908, *viii*, **15**, 499),

$$\underset{\beta}{C_6H_5.CO.CH_2}.\underset{\alpha}{CHCl}.COOH,$$

it can be said that addition through ionic and radical mechanism, both, will be effected in the α-position of β-benzoylacrylic acid.

In the above coupling reactions a certain amount of dimeric form of chalkones as well as traces of other non-nitrogenous matter of yet unidentified nature also seem to be formed, which are being investigated

EXPERIMENTAL

Coupling of p-*Chlorobenzenediazonium Chloride with* trans -β-*Benzoylacrylic Acid*

p-Chloroaniline (0.025 *M*, 3.18 g.) was dissolved in 25% HCl (0.0675*M*, 10 g.) and diazotised with 95.3% sodium nitrite (0.025 *M*, 1.90 g.), dissolved in water (5 c.c.). The diazotised solution was filtered through glass wool and added with stirring to a solution of β-benzoylacrylic acid (0.025*M*, 4.4 g.) in acetone (.0 c.c.) and containing also sodium acetate (0.073 *M*, 10 g.) and cupric chloride (1 g.) in water (2 c.c.). The mixing of the reagents was done at ordinary temperature (17°) but the temperature later was maintained below 30°. The gases evolved during the reaction were scrubbed through a saturated barium hydroxide solution by aspirating the closed reaction system with CO_2-free air. Barium carbonate was produced in substantial amount (0.9 g.). After keeping overnight the reaction mixture (A) separated in an aqueous phase, which was green in colour due to the presence of the copper salt, and a dark red semi-solid mass. The whole was steam-distilled to remove chlorobenzene, dichlorobenzene, chloroacetone etc. The steam-distilled mass on extraction with ether furnished an extract (B) and an ether-insoluble residue (C; 0.2 g.). The ether was removed from the extract (B) and the extracted matter digested with saturated sodium bicarbonate solution (20 c.c. × 2) leaving a tarry insoluble matter (D). The bicarbonate extract was cooled in ice and then acidified with ice-cold HCl. A sticky mass (E; *ca.* 3 g., moist) separated which, since it gave after some drying a deep red Pechmann dye colour on prolonged boiling with acetic anhydride, was mostly unchanged β-benzoylacrylic acid (cf. Bogert and Ritter, *J. Amer. Chem. Soc.*, 1924, **46**, 2871).

The bicarbonate-insoluble matter (D) was further treated with 2*N* alkali from which acidification produced only a slight precipitate, but no coupling product could be isolated. The alkali-insoluble matter amounted to about 4.2 g. When the latter was extracted with common organic solvents, only uncrystallisable tarry mass was obtained.

Use of Concentrated Potassium Bisulphite.—Since carbon dioxide was evolved during the coupling reaction, the presence of *p*-chlorochalkone was looked for using this reagent (cf. Knoevenagel and Morrisse, *loc. cit.*; Kratzl and Daubner, *loc. cit*). In a separate experiment, the reaction mixture (A, *vide supra*) was steam-distilled but instead of ether extraction after steam-distillation, the semi-solid mass was directly treated with aqueous sodium bicarbonate and cold 2*N*-alkali. The alkali-digested mass (4.6 g.) was refluxed with a freshly prepared saturated potassium bisulphite solution (*ca.* 20 c.c.) for 3 hours. Afterwards the sulphite liquor was diluted with water (20 c.c.), left for 2 hours and then filtered twice. The cold filtrate was basified with 60% NaOH solution (10 c.c.) when a yellow solid (1.8 g.) was deposited. It was recrystallised from alcohol, m.p. 104° changing to 114°. The crystals decolorised 1% $KMnO_4$ and gave a citron-yellow colour with H_2SO_4 (conc.). These properties agree with those of *p*-chlorochalkone. (Found: C, 74.25; H, 4.82. Calc. for $C_{15}H_{11}OCl$: C, 74.22; H, 4.53 per cent). Mixed m.p. with an authentic sample of *p*-chlorochalkone was 114°. The residue (C) had a rather high m.p. (*ca.* 180°); it did not decolorise permanganate, but with concentrated sulphuric acid produced a carmine-red colour, reminiscent of a dimeric form of a chalkone (cf. Stobbe and Breamer, *J. prakt. Chem.*, 1929, *ii*, **123**, 43).

Coupling of o- *and* m-*Chlorobenzene and* p-*Bromobenzene-diazonium Chlorides with β-Benzoylacrylic Acid*

The experiments were carried out more or less in the manner of the reaction with *p*-chlorobenzenediazonium chloride. The results are listed in Table I for the sake of comparison. Carbon dioxide ($BaCO_3$, 0.5-1 g.) was evolved during the reactions. In each case, after steam-distillation the greenish aqueous liquor was decanted off the dark red semi-solid mass. The latter was treated directly with sodium bicarbonate and then with cold 2*N* alkali. The appropriate chalkones were recovered from the 2*N* alkali-digested masses by the use of saturated potassium bisulphite.

Coupling of p-, m- *and* o-*Nitrobenzenediazonium Chlorides with* trans-*β-Benzoylacrylic Acid*

The couplings were done in the usual manner and they were always accompanied with the evolution of carbon dioxide. Recovery of the chalkones from the reaction mixture with the help of the solvents was again ineffective. Also, when the 2*N* alkali-digested products were worked up with boiling aqueous potassium bisulphite, sundry other decompositions occurred (cf. Weil and Mosser, *Ber.*, 1922, **55B**, 732; D.R.P. 151134) and only traces of nitrochalkones could be recovered on treatment of the filtrates with alkali. As an alternative, extraction of the nitrochalkones was tried with sulphuric acid (cf. Vorländer *et al.*, *loc. cit.*). After removal of the acidic and phenolic bodies

with bicarbonate and alkali, coupling products were triturated with 15 c.c. of 80-85% H_2SO_4 for 2 to 3 minutes. The sulphuric acid solution was then filtered through glass wool and the filtrate collected over crushed ice. The crude chalkones were precipitated in light brown colour. These were filtered, washed thoroughly with water and dried and crystallised first from alcohol and then recrystallised from benzene.

TABLE I

$C_6H_5CO.CH=CH.C_6H_4X$ (chalkone).

M/40-Amine diazotised.	NaOH-insoluble matter.	Yield.		Properties.	Mol. formula.	Found.	Calc.
p-Chloro-aniline	4.6 g.	1.8 g.	27.3 %	Yellow needles (from alc.), m.p. 104° changing to 114° *	$C_{15}H_{11}OCl$	C : 74.25% H : 4.81	74.22% 4.53
m-Chloro-aniline	4.8	0.3	4.6	Yellow crystals (from (dil. alc.), ** m.p. 74°	$C_{15}H_{11}OCl$	C : 73.55 H : 4.23	74.22 4.53
o-Chloro-aniline	4.8	0.3	4.6	Oil; purified by distillation under reduced pressure, † m.p. 51°.	$C_{15}H_{11}OCl$	...	...
p-Bromo-aniline	5.0	1.2	16.6	Yellow crystals (from methyl alcohol), m.p. 123 ‡	$C_{15}H_{11}OBr$	C : 62.13 H : 4.03	62.10 3.83

* Walther and Ratze, *J. prakt. Chem.*, 1902, *ii*, **65**, 280; Weitz and Scheffer, *Ber.*, 1921, **54**, 2329, footnote 1; Raiford and Davis, *J. Amer. Chem. Soc.*, 1928, **50**, 161, footnote.

. Eaton, Black and Fuson, *J. Amer. Chem. Soc.*, 1934, **53, 688.

† Weitz and Scheffer, *loc. cit.*

‡. Weygand, *Annalen*, 1927, **459**, 118.

TABLE II

$C_6H_5.CO.CH=CH.C_6H_4.NO_2$ (chalkone).

M/40-Amine diazotised.	NaOH-insoluble matter.	Yield.		Propreties	Mol. formula.	Found.	Calc.
p-Nitro-aniline	5.0 g.	1.2 g.	19%	Plates, m.p. 158-60° *. Mixed m.p. with authentic sample, 162°.	$C_{15}H_{11}O_3N$	C : 70.63% H : 4.51	71.15% 4.35
m-Nitro-aniline	4.2	0.9	14	Yellow needles, † m.p. 142-43°; mixed m.p. with authentic sample, 142°.	$C_{15}H_{11}O_3N$	C : 71.12 H : 4.53	71.15 4.35
o-Nitro-aniline	2.0	0.9	14	Light brown cryst., m.p. ‡ 122-24°.	$C_{15}H_{11}O_3N$	...	...

Wieland, *Ber.*, 1904, **37**, 1149.
Bedforss, *Ber.*, 1916, **49**, 2801.
Sorge, *Ber.*, 1902, **35**, 1067.

The sulphuric acid method of extraction was tried in reactions with *p*- and *o*-chlorobenzenediazonium chlorides also. *p*-Chlorochalkone (1.4 g.) and *o*-chlorochalkone (0.5 g.) could be recovered but the former was obtained pure after two or three crystallisations from alcohol. Also, in the purification of the *o*-chlorochalkone by distillation under reduced pressure considerable charring occurred.

Coupling of various Diazonium Chlorides with cis-*Benzoylacrylic Acid*

cis-β-Benzoylacrylic acid could be obtained from *trans*-β-benzoylacrylic acid, adopting the procedure of Lutz *et al.* (*J. Org. Chem.*, 1948, **13**, 284). The *trans*-acid (4.4 g.) in acetone (132 c.c.), when irradiated with a 100 watt lamp for 24 hours, furnished on evaporation a white powder which crystallised out from benzene in colorless needles, m.p. 84.5°, corresponding to the *cis*-acid. For effecting the coupling reaction, however, the above acetone solution of *cis*-benzoylacrylic acid, after irradiation for 24 hours, was actually concentrated to about 25 c.c., the volume used in such condensations. The reactions were done with *p*- and *m*-chloro-, *p*-bromo- and *p*-, *m*- and *o*-nitrobenzenediazonium chlorides. The reactions started with effervescence which was more brisk than noticed in reactions with *trans*-β-benzoylacrylic acid and it lasted for 1 hour only. The speed of the reaction was moderated by mixing the reagents at 0° and gradually letting the temperature rise to 25°-30°. When the evolved gases were scrubbed through barium hydroxide solution, barium carbonate was obtained. Extraction with sodium bicarbonate, followed by acidification, gave impure and unchanged benzoylacrylic acid (*vide supra*). No coupling product was obtained by extracting the bicarbonate-insoluble matter with 2 *N*-alkali and subsequent acidification. From the alkali-digested material, however, chalkones could be recovered with aqueous potassium bisulphite in the case of the halogen compounds, and 80-85% H_2SO_4 in the case of the nitrochalkones in the manner described before.

TABLE III

$C_6H_5CO.CH=CH.C_6H_4.X$ (chalkone)

M/40-Amine diazotised.	Yield.	M.P.	Mixed m p with the chalkone from the *trans*-isomer.
p-Chloroaniline	1.9 g.	114°	X = *p*-Cl 114°
m-Chloroaniline	0.3	*74°	= *m*-Cl 73-74°
p-Bromoaniline	1.3	122°	= *p*-Br 122-23°
p-Nitroaniline	1.0	160°	= *p*-NO_2 158-60°
m-Nitroaniline	0.8	*140	= *m*-NO_2 140-41°
p-Nitroaniline	0.6	123°	= *o*-NO_2 122-2.°

* Sometimes the m.p. was low by about 15° but raised itself to the stated values on keeping and without further purification.

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GIBLING'S CORRECTIONS. PART I

By A. M. Talati *

Group parachor values for the groups (C) CH_2OH, $(C)_2CHOH$ and $(C)_3COH$ have been evaluated from the parachor values of aliphatic alcohols (ethyl, *iso*propyl and *tert.*-butyl respectively). The results indicate that the interference correction for C—C—O is the same as that derived by Gibling for C—C—C. They also provide evidence in support of Gibling's assumption that the parachor values for $CH_3(C)$ and $CH_3(O)$ are the same. The parachor values for the group (C)OH is also suggested.

Gibling (*J. Chem. Soc.*, 1941, 299, 306), in an attempt to obtain parachor values in close agreement with the observed values, introduced a method of evaluating the parachors, utilising group parachors and applying certain corrections, instead of using atomic and structural constants. He maintains that the volume contribution of a given atom will vary with the nature of the atom to which it is linked and that allowance should be made for the interference which is bound to occur when atoms, though not directly united, are nevertheless brought into close conjunction as in such groupings as C—C—C and C—C—O. He believes that the change in the structure not only from $CH_2=$ to $CH\equiv$ (as observed by Mumford and Phillips, *ibid.*, 1928, 155 ; 1929, 2112) but also from CH_3-to $CH_2=$ involves a negative correction. These corrections which account for the 'branching effect' in the compounds have been termed by him as "interference corrections". He has suggested the interference corrections for C—C—C, C—C—N, C—C—O and C—C—S as 2.2, 2.4, 2.6 and 2.7 respectively (*ibid.*, 1941, 304; 1942, 661, 665 ; 1943, 14; 1944, 383) and has accounted for the interference effect in paraffins in a later paper (*ibid.*, 1945, 236). Further, he has arbitrarily allotted $CH_3(O)$ and $CH_3(N)$ the same value as for $CH_3(C)$, but has suggested different values for $(C)CH_2(C)$, $(C)CH_2(O)$ and $(C)CH_2(N)$. It is attempted here to arrive at the values of the interference corrections for the various groups by a rational method adopted by Gibling in the case of C—C—C, and to see how far his assumptions are in accordance with the evidence that will be presented in this series of papers.

Gibling derived the group parachor value for the group $(C)CH_2(O)$ as 39.4 from the parachor values of ethers and esters, and hence suggested that the interference correction for C—C—O should be 2.6. He also derived the group parachor value for the group (C)OH as 39.2 from the parachor values of methyl and ethyl alcohols by extrapolation method.

In the present paper group parachor values for the groups $(C)CH_2OH$, $(C)_2CHOH$ and $(C)_3COH$ have been derived from the mean of the parachor values, observed in the temperature range of 20° to 40° of ethyl, *iso*propyl and *tert.*-butyl alcohols respectively. "E. C." and the group parachor value for the group $(C)CH_3$, suggested by Gibling, are used in the calculations.

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The mean of the observed parachor values of ethyl alcohol (Sugden, *ibid.*, 1924, **125**, 32 ; Vogel, *ibid.*, 1948, 1815 ; Bhatnagar and Singh, *J. chim. phys.*, 1928, **25**, 21) is 127.9 From this the group parachor value for the group $(C)CH_2OH$ may be calculated as 72.6.

The mean of the observed parachor values for the *tert.*-butyl alcohol, observed by Mme. Hennant-Roland and Lek (*Bull. Soc. Chim. Belg.*, 1931, **40**, 177) and Müller (*Fet. Seifen*, 1942, **49**, 572) is 201.2. Hence, the group parachor value for the group $(C)_3$ COH will be 35.2.

The mean of the observed parachor values for methanol (Vogel, Müller, and Mme. Hennant-Roland and Lek, *loc. cit.*) may be taken as 88.0.

These values are presented in Table I, together with those for the groups (C) CH_3, $(C)_2CH_2$, $(C)_3CH$ and $(C)_4C$, as derived by Gibling (*loc. cit.*).

TABLE I

Group or compound.	[P].	Diff.	Group.	[P]	Diff.
CH_3OH	88.0	...	$CH_3(C)$	55.2	...
(C) CH_2OH	72.6	15 4	$CH_2(C)_2$	39.8	15 4
$(C)_2$ CHOH	55.0	17.6	$CH(C)_3$	22.2	17.6
$(C)_3$ COH	35.2	19.8	$C(C)_4$	2 4	19.8

The group parachor value for the group $(C)_2CHOH$ is suggested as 55.0 in the table. The actual value of the group, as found from the parachor value of *iso*propyl alcohol observed by Vogel (*loc. cit.*), is 53.8, which is lower by 1.2 than the suggested value.

It is seen from the results that the differences between the parachor values of the successive groups show a constant increment of 2.2 in both series. From these values the group parachor value for the group (C)OH may be derived as 32 8 and the interference correction for C—C—O as 2.2 in the case of alcoholic groups, if the parachor value of hydrogen is taken as 13.2, as derived by Gibling in the case of hydrocarbons (*J. Chem. Soc.*, 1945, 236).

These results also provide evidence in support of Gibling's assumption that the parachor value of $CH_3(O)$ is the same as that of $CH_3(C)$.

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CHLORAMINE -B AS A VOLUMETRIC REAGENT. DETERMINATION OF METALS

By Apar Singh

Quantitative estimations of Cu, Hg, Zn, Cd and Bi have been made with Chloramine-B as a volumetric reagent.

In the present investigation, quantitative estimations of copper, mercury, zinc, cadmium and bismuth have been made using Chloramine-B as a volumetric reagent.

In all titrations with Chloramine-B, the same procedure was adopated as in a previous communication (this *Journal*, 1954, **31**, 647). In the following tables the iodine monochloride method will be referred to as method A, the iodine cyanide procedure as B, and iodine bromide method as C.

Experimental

Determination of Copper: First Method.—A known weight of copper sulphate was dissolved in water and the solution saturated with sulphur dioxide. The solution was boiled and to it was added an excess of 10% ammonium thiocyanate slowly with constant stirring to precipitate cuprous thiocyanate. The precipitate was left to settle, filtered and washed with 10% ammonium sulphate solution till the precipitate was free from ammonium thiocyanate. The precipitate along with the filter paper was put into a stoppered conical flask. To it was added 5 c.c. of iodine monochloride and the mixture was allowed to stand for about five minutes to complete the oxidation. The liberated iodine was oxidised with standard Chloramine-B to iodine monochloride, iodine cyanide or iodine bromide in the presence of concentrated hydrochloric acid, hydrocyanic acid and a saturated solution of potassium bromide respectively.

Cuprous thiocyanate reacts with Chloramine-B as :

$$Cu_2(CNS)_2 + 7C_6H_5SO_2N\begin{matrix}Na\\Cl\end{matrix} + 8H_2O \longrightarrow 7C_6H_5SO_2NH_2 + 7NaCl + 2CuSO_4 + 2HCN.$$

Hence, 7 C.B $\equiv$ $Cu_2(CNS)_2$ $\equiv$ $2CuSO_4,5H_2O$ $\equiv$ 2Cu.

Several titrations were performed and from the volume of the standard Chloramine-B solution used, the amount of copper sulphate, and hence copper, was calculated. The results are recorded in Table I.

Table I

$CuSO_4,5H_2O$ taken.	$CuSO_4,5H_2O$ found by methods			Calc. Cu by methods		
	A.	B.	C.	A.	B.	C.
0.0320 g.	0.0327 g.	0.0327 g.	0.0327 g.	0.0083 g.	0.0083 g.	0.0083 g.
0.0400	0.0403	0 0407	0.0403	0.0103	0.0105	0.0103
0 0700	0 0702	0.0702	0.0702	0.0178	0.0178	0 0178
0.0470	0.0472	0.0476	0.0476	0.0120	0.0121	0.0121

c.c. of 0.102N C.B $\equiv$ 0.003636 g. $CuSO_4,5H_2O \equiv$ .0009253 g. Cu.

Second Method.—The method is based on the precipitation of copper from a copper salt in neutral or slightly acidic solution as copper mercury thiocyanate with a reagent containing 39.0 g. of potassium thiocyanate and 27.0 g. of mercuric chloride per litre.

$$CuSO_4 + K_2[Hg(CNS)_4] \longrightarrow K_2SO_4 + Cu[Hg(CNS)_4]$$

The greenish yellow precipitate of copper mercury thiocyanate reacts with Chloramine-B as:

$$Cu[Hg(CNS)_4] + 12C_6H_5SO_2N\langle^{Na}_{Cl} + 16H_2O \longrightarrow 12C_6H_5SO_2NH_2 + 12NaCl + CuSO_4 + HgSO_4 + 4HCN + 2H_2SO_4.$$

Hence, 12 C.B $\equiv$ $Cu[Hg(CNS)_4] \equiv CuSO_4,5H_2O \equiv Cu$.

A known weight of copper sulphate was dissolved in water and treated with an excess of potassium mercury thiocyanate. On stirring the mixture, a yellowish green precipitate of copper mercury thiocyanate was slowly formed. It was allowed to stand overnight, filtered through a weighed Gooch crucible and dried to a constant weight in an electric oven at 105°. The dry precipitate was transferred into a titration flask and dissolved in excess of hydrochloric acid. To it was added 5 c.c. of iodine monochloride and the iodine liberated was titrated against standard Chloramine-B solution. Results of the titrations are shown in Table II.

TABLE II

$CuSO_4.5H_2O$ taken.	0.1*N*-C.B used.	$CuSO_4,5H_2O$ found.	Calc. Cu.
0.0260 g.	25.30 c.c.	0.0263 g.	0.00668 g.
0.0175	17.00	0.0176	0.00449
0.0312	30.00	0.0312	0.0079
0.0156	15.50	0.0161	0.00405

1 c.c. of 0.1*N*-C.B. $\equiv$ 0.00104 g. of $CuSO_4,5H_2O \equiv$ 0.000264 g. of Cu.

Determination of Mercury: First Method.—Chloramine-B reacts with mercurous chloride in the presence of HCl according to the equation,

$$C_6H_5SO_2N\langle^{Na}_{Cl} + Hg_2Cl_2 + 2HCl \longrightarrow C_6H_5SO_2NH_2 + NaCl + 2HgCl_2.$$

Hence, 1 C. B $\equiv$ $Hg_2Cl_2 \equiv 2HgCl_2 \equiv 2Hg$.

A known weight of mercuric chloride was taken in a flask and dissolved in distilled water and to it were added 2 c.c. of pure *N*-HCl and excess of 50% phosphorous acid solution. The solution was stirred and allowed to stand for almost 12 hours. The precipitated mercurous chloride was filtered, washed with cold water and transferred along with the filter paper into a conical flask. To it was added 5 c.c. of iodine monochloride and titrated against standard Chloramine-B according to methods A and C. Method B is not applicable because of the failure of the iodine-starch reaction. Results of the titrations are summarised in Table III.

TABLE III

$HgCl_2$ taken.	$HgCl_2$ found by methods			Calc. Hg by methods		
	A.	B.	C.	A.	B	C
0 2698 g.	0.2702 g.	...	0.2716 g.	0.1996 g.	...	0.2006
0 3680	0.3666	...	0.3694	0.2708	...	0.2728
0 4278	0 4264	...	0.4291	0 3149	...	0.3169

1 c.c. of 0.1 *N*-C.B. ≡ 0.02716 g. of $HgCl_2$ ≡ 0 02005 g. of Hg.

Second Method.—Mercury can also be estimated as mercuric zinc thiocyanate which reacts with Chloramine-B in the presence of HCl.

$$Hg[Zn(CNS)_4] + 12C_6H_5SO_2N\begin{matrix}Na\\Cl\end{matrix} + 16H_2O \longrightarrow 12C_6H_5SO_2NH_2 + 12NaCl + ZnSO_4 + HgSO_4 + 4HCN + 2H_2SO_4.$$

Hence, 12 C.B ≡ $Hg[Zn(CNS)_4]$ ≡ $HgCl_2$ ≡ Hg.

The precipitating reagent was prepared by dissolving 39.0 g. of potassium thiocyanate and 29.0 g. of zinc sulphate in one litre of water. A known weight of mercuric chloride was dissolved in water and the solution was mixed with an excess of the precipitating reagent. The precipitate of mercuric zinc thiocynate was filtered, washed and titrated against standard Chloramine-B as before. Titration results are recorded in Table IV.

TABLE IV

$HgCl_2$ taken.	$HgCl_2$ found by methods			Calc Hg by methods		
	A.	B.	C.	A.	B.	C.
0.0233 g.	0.0231 g	...	0.0231	0.0170	...	0.0170 g.
0.02796	0.0271	...	0 0278	0.0205	...	0.0206
0.03728	0.0370	...	0.0375	0.0274	...	0 0277

1 c.c. of 0.103 *N*-C B. ≡ 0.001165 g. of $HgCl_2$ ≡ 0.0008608 g. of Hg.

Determination of Zinc.—Zinc is estimated as zinc mercury thiocyanate which reacts with Chloramine-B in presence of HCl according to the equation given above under the estimation of Hg. The precipitating agent, potassium mercury thiocyanate, was prepared by dissolving 39.0 g. of KCNS and 27 g. of mercuric chloride in a litre of water.

A known weight of zinc sulphate was dissolved in water and an excess of the reagent was added to it. Zinc mercury thiocyanate precipitate was washed, filtered, dissolved in hydrochloric acid and titrated against standard Chloramine-B by the method A. Results are shown in Table V.

TABLE V

$ZnSO_4, H_2O$ taken.	0.1 *N*-C.B used.	$ZnSO_4, H_2O$ found.	Calc. Zn.
0.0098 g.	14.00 c. c.	0.0104 g.	0.0038 g.
0.0142	19.80	0 0148	0.0054
0.0173	23.00	0.0172	0.0063

12 C.B. ≡ Zn $[Hg(CNS_4)]$ ≡ $ZnSO_4,H_2O$ ≡ Zn.

1 c c. of 0.1 *N*-C.B. ≡ 0.000747 g. $ZnSO_4,H_2O$ ≡ 0.0002724 g. Zn.

Determination of Cadmium .—The method is based on the precipitation of cadmium from a cadmium salt as the naphthaquinoline salt of cadmium hydroiodide $(C_{13}H_9N_2).H_2(CdI_4)$ and the iodide in the precipitate is titrated with standard Chloramine-B solution by the method B (Berg and Wurm, *Ber.*, 1927, **60**, 1664).

The iodide present in the naphthaquinoline salt of cadmium hydroiodide reacts as follows.

$$H_2(CdI_4) + 4C_6H_5SO_2N(Na)Cl + 2HCl + 4HCN \longrightarrow 4C_6H_5SO_2NH_2 + 4NaCl + CdCl_2 + 4ICN$$

Hence, 4 C.B $\equiv$ $[(C_{13}H_9N)_2.\ H_2(CdI_4)] \equiv Cd(NO_3)_2,\ 4H_2O \equiv Cd$.

A known weight of cadmium salt was dissolved in water and the solution treated with 50 c.c. of 2*N*-H_2SO_4, 50 c.c. of 10% sodium tartrate solution and sufficient 2.5% β-naphthaquinoline in 0.5*N*-H_2SO_4. To it were added a few drops of sulphurous acid solution, and the cadmium completely precipitated with 0.2*N*-KI solution. The suspension was allowed to stand for half an hour and the precipitate sucked as dry as possible and washed 2 to 3 times with a freshly prepared mixture of 10 c.c. of the 2.5% naphthaquinoline solution in 0.5*N*-H_2SO_4 diluted to 90 c.c. with water and 10 c.c. of 0.2*N*-KI. The precipitate was sucked dry again and decomposed with 20 c.c. of 2*N*-NaOH or NH_4OH. The solution was acidified with HCl and titrated against standard Chloramine-B solution by the method B. The results are recorded in Table VI.

TABLE VI

$Cd(NO_3)_2,\ 4H_2O$ taken.	Vol. of 0.1*N*-C.B used.	$Cd(NO_3)_2,\ 4H_2O$ found.	Calc. Cd.
0.0308 g.	8.40 c.c.	0.0324 g.	0.0118 g
0.0463	12.10	0.0466	0.0170
0.0578	14.90	0.0574	0.0209
0.0655	17.20	0.0663	0.0242
0.0771	20.20	0.0778	0.0284

1 c.c. of 0.1 *N*-C.B. $\equiv$ 0.003855 g. $Cd(NO_3)_2,\ 4H_2O \equiv$ 0.001405 g. Cd.

Second method is based on the precipitation of cadmium as cadmium oxinate with an alcoholic solution of 8-hydroxyquinoline, and the oxine present in the precipitate is brominated to 5 : 7-dibromohydroxyquinoline with standard Chloramine-B and excess of KBr in acid solution (by the excess method; cf. A. Singh, this *Journal*, 1954, **31**, 605).

A known quantity of the salt was dissolved in water, 3-5 g. of ammonium acetate and acetic acid were added and the solution warmed to 60°. A slight excess of a 2 % solution of oxine in alcohol was added to precipitate the cadmium oxinate. The mixture was boiled and allowed to cool. The oxinate precipitate was filtered through a sintered glass crucible, washed with hot water and dissolved in warm hydrochloric acid. About 10 c.c. of 20% KBr and a known excess of standard Chloramine-B solution were added and the solution largely diluted with 2 *N*-HCl. 40% KI (5 c.c.) was then added to the solution and the liberated iodine was titrated against standard sodium thiosulphate, using starch as the indicator.

TABLE VII

Substance taken	0.127*N*-C.B. used.	0.100*N*-$Na_2S_2O_3$, $5H_2O$ used.	0.127*N*-C B. used.	Substance found.	Calc. Cd.
0 0233 g.	20.00 c.c	18.35 c.c.	5.55 c c.	0.0236 g.	0.0010 g.
0.0333	20.00	15.35	7.91	0 0335	0.0141
0.0565	20 00	8.30	13 46	0 0569	0.0240
0.0766	27.00	11.30	18.10	0.0766	0 0323

1 c.c. 0.127*N*-C.B≡0.00433 g. of $Cd(CH_3COO)_2$, $2H_2O$≡0.00178 g. of Cd.

Determination of Bismuth.—Bismuth can also be estimated as bismuth oxinate and the oxine present in the precipitate is brominated to 5:7-dibromo-8-hydroxyquinoline with a standard Chloramine-B solution and excess of KBr in acid solution as above.

Bismuth oxinate was precipitated from the salt solution with a saturated alcoholic solution of oxine in presence of acetic acid and 1-2 g. of ammonium acetate. The results are recorded in Table VIII.

TABLE VIII

$Bi(NO_3)_3$, $5H_2O$ taken.	0.1*N*-C B added.	0.1*N* $Na_2S_2O_3$ used.	0.1*N*-C B used.	$Bi(NO_3)_3.5H_2O$ found.	Bi calc.
0 0412 g.	20.00 c c.	9.70 c c.	10.30 c.c.	0.0416 g.	0 0179 g.
0 0526	25 00	12.00	13 00	0.0525	0.0226
0.0606	25 00	9 90	15 10	0.0610	0 0279
0 0848	30.00	9.20	20.80	0.0841	0.0362

1 c.c 0 1*N*-C.B≡0.00404 g $Bi(NO_3)_3$, $5H_2O$≡0.00174 g. Bi.

Second method is based on the fact that bimsuth is precipitated as oxyquinoline salt of bismuth hydroiodide [$(C_9H_7ON)\ H_2(BiI_4)$] and the iodide in the precipitate reacts quantitatively with standard Chloramine-B solution in presence of HCN, according to the equation given above under the estimation of cadmium.

A known weight of bismuth nitrate was dissolved in water. It was slightly acidified with nitric acid and treated with an excess of 5% solution of oxyquinoline in 0.2*N*-H_2SO_4. Approximately 0.1*N*-KI solution was dropped in until the precipitate of the oxyquinoline salt of bismuth hydroiodide was granular. The precipitate was filtered at once and washed with a wash liquid of the following composition: 50 c.c. of 2*N*-H_2SO_4, 25 c.c. of 0.1*N*-KI, 1.8 g. of oxyquinoline and a pinch of hydrazine sulphate, dissolved and made up to one litre. The washed precipitate was sucked dry, dissolved in 10% HCl and titrated with standard Chloramine-B solution in presence of HCN as described above. The results are shown in Table IX.

TABLE IX

$Bi(NO_3)_3, 5H_2O$ taken.	0.106*N*-C.B used.	$Bi(NO_3)_3, 5H_2O$ found.	Bi calc.
0.0606 g.	9.40 c.c.	0.0604 g.	0.0260 g.
0.0909	14.20	0.0912	0.0393
0 1507	16.40	0.1054	0.0454
0 1278	20 00	0.1285	0.0554
0.0788	12 30	0.0790	0.0341

1 c.c. of 0.106 *N*-C.B≡0.006425 g. $Bi(NO_3)_3, 5H_2O$≡0.002769 g. of Bi.

From the above it is evident that copper, mercury, zinc, cadmium and bismuth can be estimated quantitatively using Chloramine-B as a volumetric reagent.

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RELATION BETWEEN TOTAL AND INTERNAL LATENT HEATS OF EVAPORATION OF LIQUIDS

By Surendra Nath Srivastava and Yatendra Pal Varshni

If λ and L be the internal and total heats of evaporation, it is shown that $\lambda = AL^B$, where A and B are constants.

Numerous formulae have been suggested for the variation of internal and total latent heats of evaporation with temperature, and it has been said that latent heat is "a quantity which is peculiarly adaptable to representation by empirical formulae" (Partington, "An Advanced Treatise on Physical Chemistry, Properties of Liquids", Longmans Green & Co., p. 319). However, no attempt seems to have been made to find a relation between λ and L only (λ represents internal latent heat of evaporation and L, total latent heat of evaporation). The present paper suggests such a relationship.

Kendall (*J. Amer. Chem. Soc.*, 1914, **36**, 1620), Winter (*J. Phys. Chem.*, 1928, **32**, 576), Thiesen (*Physikal. Z.*, 1911, **12**, 321), De Hemptinne (*Bull. Acad. Roy. Belg.*, 1926, **12**, 296), De Wijs (*Rec. trav. chim.*, 1943, **62**, 449, 445 ; *J. Phys. Chem.*, 1950, **54**, 599), Nesselmann and Dardin (*Wiss. Veroff. Siemeiss Kozern*, 1931, **10**, 129), Bowden and Jones (*Phil. Mag.*, 1946, **37**, 480) and others have represented the variation of L with temperature by formulae of the form

$$L = L_o (T_c - T)^m \quad \ldots \quad \ldots \quad (1)$$

where T_c and T represent critical and absolute temperature respectively, m (a const.) $\approx$0.4 and L_o, a constant.

On the other hand, the variation of the internal latent heat has also been represented by similar formulae by Van Laar ("Die Zustandsgleichung", 1924, p. 263), Bowden and Jones (*loc.cit.*) and others.

$$\lambda = \lambda_o (T_c - T)^n \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Eliminating $(T_c - T)$ between equations (1) and (2) we get

$$\left(\frac{\lambda}{\lambda_o}\right)^{1/n} = \left(\frac{L}{L_o}\right)^{1/m}$$

which becomes

$$\lambda = AL^B \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

on putting A for $\lambda_o / L_o^{\frac{n}{m}}$ and B for n/m, where A, B, λ_o, L_o, m and n are constants.

Equation (3) has been tested on various liquids. The relation is found to hold for non-associated as well as associated liquids over wide temperature ranges. Results for three typical liquids, viz., *n*-hexane, water and ethyl alcohol, are shown in Tables I, II, and III respectively. The values for the constants for 36 liquids on which the formula has been tested, are recorded in Table IV.

TABLE I

n-Hexane (non-associated).

$\lambda = 0.6774.L^{1.066}$.

Temp.	$L_{obs.}$	$\lambda_{obs.}$	$\lambda_{calc.}$	%Error.
0°	90.98	84.68	82.91	2.1
60°	80.82	73.59	72.73	1.2
80°	77.55	70.04	69.97	0.1
100°	73.48	65.82	66.04	0.3
120°	69.29	61.56	62.06	1.0
140°	63.84	56.29	56.86	1.0
160°	57.63	50.45	50.98	1.0
180°	50.93	44.30	44.67	0.8
200°	42.75	37.00	37.08	0.2
220°	30.37	26.18	25.76	1.6
230°	19.73	16.98	16.64	2.0
234°	10.41	8.98	8.25	8.1

TABLE II

Water (associated).

$\lambda = 0.2672.L^{1.198}$.

Temp.	$L_{obs.}$	$\lambda_{obs.}$	$\lambda_{calc.}$	%Error.
0°	595.8	565.0	56[illegible].6	0.25
20°	584.8	552.5	551.3	0.14
40°	573.5	539.2	542.0	0.52
60°	561.8	525.4	525.8	0.02
80°	549.8	511.4	510.9	0.01
100°	537.5	497.1	498.3	0.24
120°	523.0	481.0	482.1	0.23
140°	508.5	465.0	465.9	0.19
160°	494.2	449.2	450.6	0.31
180°	479.7	433.6	434.7	0.26
200°	465.3	418.2	419.2	0.25
220°	449.4	402.1	402.1	0.00
240°	429.5	381.7	380.72	0.26
260°	402.5	355.7	351.6	1.15
270°	390.3	344.7	339.6	1.45

TABLE III

Ethyl alcohol (highly associated).

$\lambda = 0.6327.L^{1.073}$.

Temp.	0°	20°	40°	60°	80°	100°	120°	140°	160°	180°	200°	220°
$L_{obs.}$	220.9	220.6	218.7	213.4	206.4	197.1	184.2	171.1	156.9	139.2	116.6	88.2
$\lambda_{obs.}$	209.2	208.0	205.3	199.2	191.6	181.8	168.8	155.7	141.7	124.9	104.0	78.3
$\lambda_{calc.}$	207.6	207.3	205.3	199.9	192.9	183.7	170.8	155.7	143.7	126.4	101.5	77.5
%Error	0.80	0.34	0.0	0.35	0.67	1.04	1.20	0.0	1.4	1.2	0.50	1.02

TABLE IV

Sr. No.	Liquid.	Temp. range.	*A*.	*B*.	(Average) % Error.	Sr. No.	Liquid.	Temp. range.	*A*.	*B*.	(Average) % Error.
1	Ethyl ether	0°-193°	0.6699	1.068	1.2	19	Methyl butyrate	0°-280°	0.6630	1.073	1.3
2	Di-*iso*propyl ...	0°-225°	0.6237	1.085	1.0	20	Methyl *iso*butyrate	0°-266°	0.6441	1.080	1.3
3	Di *iso*butyl ...	0°-274°	0.6823	1.058	1.1	21	Methyl alcohol	0°-238°	0.6295	1.069	0.8
4	*iso*Pentane	0°-187°	0.6138	1.086	1.2	22	Ethyl alcohol	0°-220°	0.6327	1.073	
5	*n*-Pentane	0°-197°	0.6607	1.068	1.1	23	Acetone	0°-100°	0.2875	1.237	0.5
6	*n*-Hexane	0°-234°	0.6774	1.066	1.0	24	SO_2	−10°-155°	0.6751	1.064	1.1
7	*n*-Heptane	0°-266°	0.6372	1.081	1.0	25	Ammonia	−30°- 40°	0.2677	1.213	0.07
8	*n*-Octane	0°-280°	0.6926	1.064	1.0	26	CO_2	−30°- 30°	0.7582	1.032	0.5
9	Benezne	0°-280°	0.5936	1.092	1.1	27	Nitrous oxide	−25°- 30°	0.8606	0.9893	1.2
10	Fluorobenzene	0°-280°	0.6201	1.086	0.95	28	Chloroform	0°-100°	0.3247	1.250	0.09
11	Chlorobenzene	0°-270°	0.4679	1.152	1.1	29	Ethyl acetate	0°-249°	0.7106	1.054	0.85
12	Bromobenzene	30°-270°	0.4554	1.172	0.5	30	Propyl alcohol	0°-260°	0.6707	1.064	0.8
13	Iodobenzene	30°-270°	0.4218	1.200	0.17	31	CS_2	0°-150°	0.3847	1.192	0.25
14	CCl_4	0°-280°	0.6492	1.085	1.2	32	Methyl propionate	0°-256°	0.6833	1.069	2.4
15	$SnCl_4$	0°-280°	0.6476	1.099	0.76	33	Propyl formate	0°-260°	0.6818	1.064	1.1
16	Ethyl formate	0°-234°	0.6639	1.068	1.1	34	Methyl acetate	0°-233°	0.6705	1.067	1.2
17	Propyl acetate	0°-275°	0.6858	1.065	1.1	35	Methyl formate	0°-270°	0.6619	1.065	1.1
18	Ethyl propionate	0°-270°	0.7056	1.058	1.1	36	Water	0°-270°	0.2672	1.198	0.27

Latent heat data have been taken from Mills (*J. Amer. Chem. Soc.*, 1909, **31**, 1099), and five figure tables have been used for calculatons. In most of the cases the range extends from zero degree centigrade to very near the critical temperatures of the respective liquids. It will be noticed that the agreement between the observed and calculated values is satisfactory.

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NITROMETRIC ESTIMATION OF SILVER NITRITE AND STRONTIUM NITRITE IN ADMIXTURE WITH THE HYPONITRITES

By T. M. Oza, V. T. Oza and G. T. Oza

The nitrometric estimation of nitrites in admixture with hyponitrites in the case of the sodium and calcium salts has been reported by Oza, Oza and Dipali (this *Journal*, 1951, **28**, 15). In the present investigation the estimation covers the mixtures of strontium nitrite-strontium hyponitrite and silver nitrite-silver hyponitrite.

Silver nitrite and silver hyponitrite were extra pure and the same as those used in the study of their thermal decomposition (Thaker, Ph. D. thesis, Gujarat University, 1954); strontium nitrite was the same as the one prepared by V. Oza after Oza and Dipali (this *Journal*, 1950, **27**, 290); strontium hyponitrite was prepared after Oza and Patel (*ibid.*, 1954, **31**, 523). These were analysed and found pure.

Procedure.—The procedure for the strontium salt was the same as that for the calcium salt (Oza, Oza and Dipali, *loc. cit.*). In the case of the silver salts, the weighed quantity of each salt, mixed together, was dissolved in ammoniacal water using as small a volume as possible; the solution was admitted into the nitrometer and the cup rinsed with 1 c.c. of water. On admitting thiourea (1 c.c.) to the solution, it turned black, and then on adding 2 c.c. of 75% acetic acid, the gas began to be evolved. As about 8 to 10 c.c. of the solution was present in the nitrometer at the end, the gas was transferred to a eudiometer over mercury and its volume measured. The results are shown below.

TABLE I

Mixture taken.		* Gas	Gas	Mixture taken.		* Gas	Gas
$SrN_2O_2,5H_2O$.	$Sr(NO_2)_2,H_2O$.	formed.	expected.	$Ag_2N_2O_2$.	$AgNO_2$.	formed.	expect d.
0.0115 g.	0.0525 g.	5.85 c.c.	5.95 c.c.	0.0050 g.	0.0554 g.	8.05 c.c.	8 06 c.c.
0.0515	0.0725	8.1	8.22	0.0110	0.0670	9 5	9.75
0.0500	0.0750	8.4	8 5	0 0181	0.0750	11.0	10.85
0.0260	0.0680	7.6	7.7	0 0320	0.0881	13.0	12.80
0.0115	0.0361	4.0	4.1	0.0251	0 1022	15.3	14.85
0.0000	0.1050	11.8	11.9	0.0000	0 0815	11.6	11.80

* Volumes of gas are at N.T.P.

The results show that the presence of hyponitrite does not interfere with the estimation of the nitrite. As hyponitrites are destroyed by boiling in solution, the mixed solution, if boiled and cooled prior to admitting to the nitrometer, it is better. Nitrites in solution can often be boiled without decomposition (P.C. Ray, *J. Chem. Soc.*, 1905, **87**, 177).

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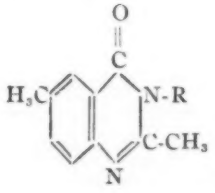
SYNTHESIS OF 2:6-DIMETHYL-3-SUBSTITUTED QUINAZOL-4-ONES

By G. S. Mewada, S. R. Patel and N. M. Shah

In extension of our work on the synthesis of Bz-nuclear substituted quinazolone derivatives (Mewada, Patel and Shah, this *Journal*, 1955, **32**, 199), 2:6-dimethyl-3-substituted-quinazol-4-ones have been synthesised by condensing 5-methyl-N-acetylanthranilic acid with different aromatic amines under the conditions similar to those used in the earlier paper (*loc.cit.*).

5-Methylanthranilic acid was synthesised from *p*-toluidine. Treatment of the latter with hydroxylamine and chloral hydrate furnished *iso*nitroso-*p*-methylacetanilide, which was cyclised to 5-methylisatin (Organic Syntheses. Coll. Vol. I, 2nd Ed., p. 330); the latter on oxidation with alkaline hydrogen peroxide yielded 5-methylanthranilic acid. This method is more facile than the reduction of 2-nitro-5-methylbenzoic acid (Findeklee, *Ber.*, 1905, **38**, 3553). The N-acetyl derivative, prepared by acetylation with acetic anhydride in benzene, was identical with the same obtained by oxidation of 2:3:6-trimethylquinoline by neutral $KMnO_4$ solution (Miller and Ohler, *Ber.*, 1891, **24**, 1910).



The procedure for condensation has been described in the earlier paper (*loc.cit.*). Hence, to avoid the repetition, the details are omitted and the quinazolones obtained and their hydrochlorides prepared are shown in Table I.

Alcohol was used throughout as a solvent except in case (2) where acetone was used. If necessary, the product was recrystallised from petroleum ether.

TABLE I

Sr.No.	-R.	M. P.	Crystalline form.	Formula.	Analysis. Found.	Calc.
1	$-C_6H_5$	124°	Rhombic crystals	$C_{16}H_{14}ON_2$	N, 10.9%	11.2%
	Hydrochloride of (1)	272°	Short needles	$C_{16}H_{15}ON_2Cl$	Equiv. 279.8	285.5
2	$-C_6H_4.OCH_3$ (-p)	148°	Long needles	$C_{17}H_{16}O_2N_2$	N, 9.81%	10.0%
	Hydrochloride of (2)	246°	Short needles	$C_{17}H_{17}O_2N_2Cl$	Equiv. 309.9	316.5
3	$-C_6H_4.Cl$ (-o)	175°	Prismatic needles	$C_{16}H_{13}ON_2Cl$	N, 9.16%	9.8%
					Cl, 12.37	12.51
	Hydrochloride of (3)	240°	Small prisms	$C_{16}H_{14}ON_2Cl_2$	Equiv. 320.2	321.5
4	$-C_6H_4.Cl$ (-m)	144°	Short needles	$C_{16}H_{13}ON_2Cl$	N, 9.45%	9.8%
					Cl, 11.98	12.51

TABLE I (*contd.*)

Sr.No.	-R.	M. P.	Crystalline form.	Formula.	Analysis. Found.	Calc.
	Hydrochloride of (4)	255-56°	Short needles	$C_{16}H_{14}ON_2Cl_2$	Equiv. 322.0	321.5
5	$-C_6H_4$- Cl (-*p*)	150°	Thick plates	$C_{16}H_{13}ON_2Cl$	N,9.6%	9.8%
					Cl, 12.26	12.51
	Hydrochloride of (5)	264-65°	Long needles	$C_{16}H_{14}ON_2Cl_2$	Equiv. 326.7	321 5
6	$-C_6H_4.CH_3$ (-*o*)	* 166°	Long needles	$C_{17}H_{16}ON_2$	N, 10.25%	10.6%
	Hydrochloride of (6)	248°	Short needles	$C_{17}H_{17}ON_2Cl$	Equiv. 302.4	300.5
7	$-C_6H_4.CH_3$ (-*m*)	125°	Prismatic needles	$C_{17}H_{16}ON_2$	N, 10.35%	10.6%
	Hydrochloride of (7)	252°	Short needles	$C_{17}H_{17}ON_2Cl$	Equiv. 296.5	300.5
8	$-C_6H_4.CH_3$ (-*p*)	136°	Thick plates	$C_{17}H_{16}ON_2$	N, 10.24%	10 6%
	Hydrochloride of (8)	262°	Small rhombic crystals	$C_{17}H_{17}ON_2Cl$	Equiv. 298.7	300.5

* Subbaram (*Proc. Ind. Acad. Sci.*, 1954, **40A**, 22) records m.p. 159-61°.

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A NOTE ON THE ISOLATION OF β-SITOSTEROL FROM *HEMIDESMUS INDICUS* *

By Ramesh Chandra Chatterjee and Bidyut Kamal Bhattacharyya

Dutta, Ghosh and Chopra (*Arch. Pharm.*, 1938, **276**, 333) investigated the roots of *Hemidesmus indicus* and claimed to have isolated two sterols. Murti and Seshadri (*Proc. Ind. Acad. Sci.*, 1941, **13A**, 399; 1941, **14A**, 93) have shown that the above two substances are a mixture of α- and β-amyrins and lupeol. Furthermore, the latter workers suspected some sterols occurring in the same roots. Present investigation deals with the isolation of β-sitosterol.

The non-saponifiable matter was chromatographed on alumina when the mixture of triterpenoid alcohols was eluted with 25% benzene in hexane, and the sterol with 50% benzene in hexane. The sterol was crystallised several times and identified as β-sitosterol. It may be mentioned that the chromatography of the benzoates of the triterpenoid alcohols furnished only α-amyrin and lupeol in very poor yield.

β-*Sitosterol*.—Powdered roots (60 mesh, 2.5 kg.) was extracted continuously with a mixture of acetone and alcohol (25 : 75 ; 3000 ml.) for 24 hours. After evaporation of the solvents the residue (115 g.) was saponified with potassium hydroxide in a mixture of ethanol and benzene, furnishing a thick viscous red oil (39 g.) as non-saponifiable matter. This oil (3.9 g.) was dissolved in dry *n*-hexane (300 ml.) and chromatographed on alumina (90 g.). The solid obtained by elution with hexane-benzene (75 : 25), m.p. 135°-160° (0.47 g.), was the mixture of triterpenoid alcohols. The semi-solid material, eluted with hexane-benzene (50:50), was crystallised repeatedly from a mixture of methanol and ethyl acetate, m.p. 135-37° (40 mg.). It was again chromatographed and then crystallised from methanol, m.p. 135°-37°; $[\alpha]_D$, −34°.95 ($CHCl_3$; *c*, 1.68). (Found : C, 83.75 ; H, 12 22. Calc. for $C_{29}H_5O$: C, 83.98 ; H, 12.15 per cent). This was benzoylated with benzoyl chloride and pyridine and the benzoate (m. p. 143°) was chromatographed following the procedure of Brooks, Klyne and Miller (*Biochem. J.*, 1953, **54**, 212) and then crystallised from ethyl acetate-methanol mixture, m. p. 145.5°, $[\alpha]_D$, −13°.8 ($CHCl_3$; *c*, 1.69). (Found : C, 83.72 ; H, 10.66. Calc. for $C_{36}H_{54}O_2$: C, 83.34 ; H, 10.49 per cent). The above sterol was converted into the acetate and the purity of the acetate was checked as in the case of benzoate, m. p. 125-27°, $[\alpha]_D$, −37°.9 ($CHCl_3$; *c*, 1.93). For further identification of β-sitosterol the absorption spectra in concentrated sulphuric acid were measured following the procedure of Bernstein and Lenhard (*J. Org. Chem.*, 1953, **18**, 1146).

λ_{max} , 314 mμ, $E^{1\%}_{1\,cm}$ (185) ; 416 mμ, $E^{1\%}_{1cm}$(73.2).

λ_{min} , 252.5 mμ, $E^{1\%}_{1cm}$ (63.2); 390 mμ, $E^{1\%}_{1cm}$ (53.2).

* The melting points are uncorrected. The ultraviolet absorption was taken in an Unicnm spectrophotometer s.p. 500.

α-Amyrin and Lupeol.— The crude triterpenoid alcohols (1.2 g.) were crystallised eight times from methanol-ethyl acetate mixture to afford two fractions of m. p. 175-78° (A ; 82 mg.) and m. p. 160-63° (B ; 435 mg.). The fraction (A) was benzoylated and the benzoate was crystallised five times from benzene-ethanol (1 : 4) mixture, m. p. 192-93°, which on hydrolysis and crystallisation furnished α-amyrin, m. p. 186-87°, $[\alpha]_D$, +81°.7 ($CHCl_3$; *c*, 1.59), identified also by direct comparison with an authentic sample. This was also converted into the acetate, m.p. 220-22°, $[\alpha]_D$, +77°.2 ($CHCl_3$; *c*, 1.61). The benzoate, m. p. 210-15°, obtained from the fraction (B), was crystallised four times from alcohol-benzene, m.p. 228-29° and then chromatographed as before, furnishing crystals, m. p. 245-46°, which was again rechromatographed and the material of m. p. 256-57° obtained thereby was first chromatographed and then crystallised from ethanol-ethyl acetate to furnish lupeol benzoate, m. p. 262-63°, $[\alpha]_D$, + 60° ($CHCl_3$; *c*, 1.7).

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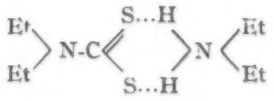
A NOTE ON THE PARACHOR OF DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE

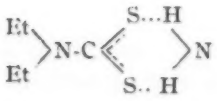
By Miss I. Bokil and C. V. Ramamruty

The diethylammonium diethyidithiocarbamate is a substance of rather unsual properties for a salt of a dithiocarbamic acid. It is almost a common product of the pyrolysis of various diethylamine-carbon disulphide class of rubber accelerators, e.g., the commercial S.D.C., Z.D.C., T.E.T, etc. It has a high molecular weight of 222 and yet it is freely soluble in most organic solvents including benzene, ether, chloroform, carbon tetrachloride and others. It can be distilled undecomposed at 125°, and on drastic heating in a sealed tube above this temperature it is partly converted into tetraethylthiocarbamide (Sahasrabudhey and Radhakrishnan, this *Journal*, 1954, **31**, 853). In view of these facts the simple salt structure (I) appears inadequate to explain its chemistry. A parachor study was therefore undertaken.

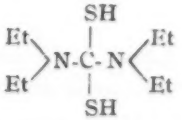
(I; $P_{calc.}$ 564.0)



(II, $P_{calc.}$ 570.1)



(III, $P_{calc.}$ 546.9)



(IV, $P_{calc.}$ 540.8)

The average parachor values for this substance range between 487 and 538; in absolute alcohol, benzene, nitrobenzene and pyridine they are 487.6, 499.8 538.6 and 520.9 respectively. The calculated value for (I) is 564. The dielectric constant of the above four solvents varies within the range of 2 to 36. The observed parachor values, however, suggest no particular dependence on this quantity or the 'nature' of the solvent as such.

The large negative anomaly observed with respect to (I) cannot be due to dissociation of the salt. It is suggested that the structures (II), (III) and (IV), which are probable, might also be making a contribution to the constitution of this substance. These structures are highly polar, and (II) and (III) besides, involve hydrogen bonds. Thus, the large negative anomaly, which is common with respect to all the four probable structures, may be due to resonance effects (Bhagwat and Shukla, *ibid.*, 1950, **27**, 283),

hydrogen bonds (Sidgwick and Bayliss, *J. Chem. Soc.*, 1930, 2027), and polar effects (Bhagwat *et al.*, this *Journal*, 1938, **15**, 43; 1944, **21**, 53, 62; 1949, **26**, 39). Such a view of the structure of this substance is in better accord with the above referred properties of the substance.

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A NOTE ON THE ALKYLATION OF AMIDES

By Kazi Abdul Latif and Md. Abdus Sattar

Pachter and Kloetzel (*J. Amer. Chem. Soc.*, 1952, **74**, 1321) methylated some amides by methyl iodide in presence of dry KOH in acetone with high yields. We have studied this reaction with a view to its applicability as a general process of alkylation of amides. The reaction has been found to be applicable for almost all types of alkyl halides, and several N-alkyl-*p*-nitroacetanilides have been prepared, as shown in Table 1.

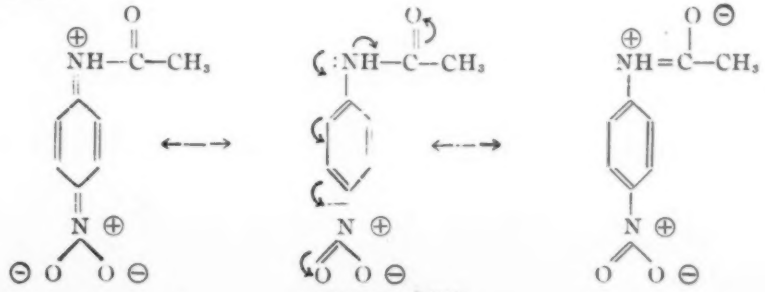
Table I

Time of reflux = 5 mins.

Alkyl group.	M. P.		% Yield.	% Nitrogen.	
	Observed.	Lit.*		Found.	Calc.
CH_3	153°	153 54°	89	...	...
C_2H_5	118-19°	118-19°	84	...	...
C_3H_7	77-78°	...	80	12 3	12.6
C_3H_5	90°	...	90	12.2	12.7
$C_6H_5CH_2$	108°	108-109°	80	...	...

However, certain limitations to this reaction have also been observed. N-Methyl-*p*-nitrobenzamide, in contrast to *p*-nitroacetanilide, did not furnish any alkylation product on refluxing for 5 minutes only. *p*-Nitrobenzamide yielded its N-methyl derivative in 50% yield only after refluxing for half an hour, whereas benzamide itself did not react at all.

The difference in the reactivity of *p*-nitroacetanilide and N-methyl-*p*-nitrobenzamide (both of them are substituted amides and also structural isomers) may be explained from their structure. In *p*-nitroacetanilide, the hydrogen atom attached to the -NH- group will be more protonic in nature than that in N-methyl-*p*-nitrobenzamide due to the combined resonance effect of the two negative groups from two sides. Hence, substitution of that hydrogen through the intermediate formation of an anion in presence of a base will be easier.



p-Nitroacetanilide.

N-Methyl-*p*-nitrobenzamide.

The above observation also indicates that those amides, either substituted or unsubstituted, may be alkylated by this process which contain fairly positive hydrogen atom or atoms.

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A NOTE ON THE CONDENSATION OF 2-IODO-3 : 5-DINITRODIPHENYL WITH SODIO-ACETOACETIC ESTER

By S. H. Zaheer and I. K. Kacker

In an earlier communication (this *Journal*, 1946, **23**, 380) condensation of 2-halo-3 : 5-dinitrodiphenyl with sodio-acetoacetic ester in the absence of any solvent was reported by us to furnish 3 : 5-dinitrodiphenyl-2-acetoacetic ester in good yield. However, certain difficulties were experienced later when the reaction was run on a larger scale.

Two experiments were attempted using 55 g. (0.15 *M*) of 2-iodo-3 : 5-dinitrodiphenyl, 39 g. (0.3 *M*) of acetoacetic ester and 6.9 g. (0.3 *M*) of sodium in a powder form suspended in dry ether (1.5 litres) contained in a three-necked flask. The reaction conditions were the same as reported earlier. Care was taken to see that no sodium was left unchanged and all the ether removed (last traces were removed under reduced pressure) before heating was commenced. The reaction mass became deeper red in colour with rise in temperature. At 90°-95°, the reaction became violent and the mass caught fire (even when an atmosphere of nitrogen was maintained) blowing off all the fittings, but it was not accompanied with any explosion.

After a number of experiments with decreasing quantities of the reactants and varying conditions, it was found possible to carry out the reaction successfully using only 5 to 6 g. of the diphenyl compound in one batch. Larger quantities than this led to uncontrollable reactions. The condensation of 2-halo-3 : 5-dinitrodiphenyl with sodio-acetoacetic ester, reported earlier by the authors (*loc. cit.*), should only be carried out with 5 to 6 g. of the diphenyl compound, as larger quantities than this lead to explosion.

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THE CONDENSATION OF AROMATIC ALDEHYDES WITH ETHYL PHENYLSULPHONYLACETATE, PHENYLSULPHONYLACETONITRILE AND ω-PHENYLSULPHONYLACETOPHENONE

By M. Balasubramanian and V. Baliah

Ethyl phenylsulphonylacetate condenses with *m*-nitrobenzaldehyde and cinnamaldehyde to furnish 1-ethoxycarbonyl-2-*m*-nitrophenyl-1 phenylsulphonylethylene and 1-ethoxycarbonyl-4-phenyl-1-phenylsulphonylbuta-1 : 3-diene respectively. Several similar αβ-unsaturated sulphones have been obtained by the condensation of phenylsulphonylacetonitrile and ω-phenylsulphonylacetophenone with aromatic aldehydes. Some aldehydes yield Mannich bases with ω-phenylsulphonylacetophenone and ammonia.

In a previous paper (*J. Chem. Soc.*, 1954, 1844) we reported that arylsulphonylacetic acids condensed with aromatic aldehydes and ammonia or amines to furnish β-amino-sulphones. The formation of αβ-unsaturated sulphones in such condensations was also reported. Ethoxycarbonyl, cyano, and keto groups have greater activating influence than a carboxyl group on the hydrogen atoms attached to the adjacent carbon atom, and hence, it was thought of interest to investigate the reaction further by employing ethyl phenylsulphonylacetate, phenylsuphonylacetonitrile and ω-phenylsuphonylacetophenone in place of the arylsulphonylacetic acid.

Ethyl phenylsulphonylacetate and phenylsulphonylacetonitrile condensed with aromatic aldehydes in the presence of ammonium acetate to afford only αβ-unsaturated sulphones of the type (I); no β-amino-sulphone could be obtained. The products obtained with ω-phenylsulphonylacetophenone and ammonia depended upon the solvent and the aldehyde used. In ethanol the results were as follows: *p*-Chlorobenzaldehyde yielded the β-amino-sulphone (II, Ar = *p*-ClC_6H_4) as well as the αβ-unsaturated sulphone. Benzaldehyde afforded the diamine (III) and the unsaturated sulphone. *m*-Nitrobenzaldehyde furnished the β-amino-sulphone (II; Ar = *m*-$O_2NC_6H_4$) only, while the other aldehydes yielded the αβ-unsaturated sulphones only. In glacial acetic acid the products were exclusively αβ-unsaturated sulphones irrespective of the aldehyde employed.

$Ph.SO_2.C(R)=CH.Ar$
[R = CO_2Et, CN or COPh]
(I)

$Ph.SO_2.CH(COPh).CH(Ar)NH_2$
(II)

$Ph.CH.NH_2$
|
$PhSO_2.C.COPh$
|
$Ph.CH.NH_2$
(III)

$CH_3CH[CH(COPh)SO_2.Ph]_2$
(IV)

$Ph.SO_2.C=CH.CH=CH.Ph$
|
CO_2Et
(V)

Several unsaturated sulphones of the type $ArSO_2.C(CN)=CHAr'$ were obtained by Tröger *et al.* (*J. prakt. Chem.*, 1908, *ii*, **78**, 123; 1922, **104**, 335; *Arch. Pharm.*, 1909, **247**, 613) by the reaction of arylsulphonylacetonitriles with aromatic aldehydes in the presence of a trace of alkali. The use of ammonium acetate in place of alkali seems to be advantageous for this reaction. The yields of the sulphones exceed 90% in most cases. Aliphatic aldehydes including chloral failed to condense with any of

the three reactive sulphones. However, acetaldehyde-ammonia condenses with ω-phenylsulphonylacetophenone to give rise to a compound whose properties and analytical data indicate structure (IV).

EXPERIMENTAL

1-Ethoxycarbonyl-2-m-nitrophenyl-1-phenylsulphonylethylene (I : R = CO_2Et, Ar = m-$O_2N.C_6H_4$).—Ethyl phenylsulphonylacetate (2.28 g.) (Ashley and Shriner, *J. Amer. Chem. Soc.*, 1932, **54**, 4410), *m*-nitrobenzaldehyde (1.51 g.) and ammonium acetate (0.77 g.) were dissolved in absolute ethanol (5 c.c.) by warming and the mixture was left aside. It became turbid and an oil gradually separated from the solution. After 24 hours, the oil set to a solid which was filtered off and washed with ethanol (6 c.c.). The yield was 2.52 g. (70%). The *sulphonylethylene* crystallised from glacial acetic acid as yellow tablets, m.p. 154-55°. (Found : C, 56.23 ; H, 4.26. $C_{17}H_{13}O_6NS$ requires C, 56.50 ; 4.16 per cent).

1-Ethoxycarbonyl-4-phenyl-1-phenylsulphonylbuta-1 : 3-diene (V) was obtained by the same method as above, using cinnamaldehyde for benzaldehyde. The yield was 29%. The product crystallised from ethanol in light yellow needles, m.p. 105-106.5°. (Found : C, 66.65 ; H, 5.39. $C_{19}H_{16}O_4S$ requires C, 66.67 ; H, 5.26 per cent).

TABLE I

αβ-Unsaturated sulphones.

$PhSO_2C(R)=CHAr$

Ar.	Yield.	Solvent.	M.P.	Formula.	% Carbon Found.	% Carbon Calc.	% Hydrogen Found.	% Hydrogen Calc.
			R = CN					
Phenyl	100%	Ethanol	137-38°*	$C_{15}H_{11}O_2NS$	...	...	...	...
Methylenedioxyphenyl	96	Acetone	170-71°	$C_{16}H_{11}O_4NS$	61.60	61.35	3.70	3.52
o-Anisyl	73	Methanol	106-107.5°	$C_{16}H_{13}O_3NS$	64.16	64.21	4.46	4.35
p-Anisyl	92	Ethanol	113-14°†	,,	...	...	...	...
o-Chlorophenyl	98	,,	134-35°	$C_{15}H_{10}O_2NClS$	59.40	59.32	3.58	3.30
p-Chlorophenyl	95	,,	155-56°	,,	59.36	59.32	3.60	3.30
p-Tolyl	62	,,	144-45°	$C_{16}H_{13}O_2NS$	67.35	67.84	4.69	4.59
m-Nitrophenyl	93	Ethanol-acetone	149-50.5°	$C_{15}H_{10}O_4N_2S$	57.24	57.33	3.50	3.19
			R = CO.C_6H_5.					
p-Tolyl	68	Ethanol	174-75.5°	$C_{29}H_{18}O_3S$	72.83	72.93	5.22	4.97
Methylenedioxyphenyl	17	Dioxan-ethanol	178-79°	$C_{22}H_{16}O_5S$	67.64	67.35	4.14	4.08
o-Anisyl	77	Dioxan-water	130-31°	$C_{22}H_{18}O_4S$	6.76	69.84	4.96	4.76
p-Anisyl	28	Ethanol	161-63°	,,	70.20	,,	5.03	,,
m-Nitrophenyl	48	Acetone	169-71°	$C_{21}H_{15}O_5NS$‡	64.43	64.12	4.01	3.84

* Tröger and Prochnow (*J. parkt. Chem.*, 1908, *ii*, **78**, 123) record m.p. 135°.

† Tröger and Prochnow (*loc cit.*) record. m.p. 113°.

‡ Obtained by refluxing for 10 minutes ω-phenylsulphonylacetophenone, *m*-nitrobenzaldehyde and ammonium acetate (0.1 mole each) in glacial acetic acid (5 c.c.) and adding ether.

Phenylsulphonylacetonitrile.—Tröger and Hille (*J. prakt. Chem.*, 1905, *ii*, **71**, 201) obtained this compound by heating a mixture of sodium benzenesulphinate and chloroacetonitrile in ethanol at 100° in a sealed tube. It has been found in the present investigation that the reaction between sodium benzenesulphinate and chloroacetonitrile could be conveniently effected by heating them in ethanol on a water-bath for 16 hours. The yield was 54%. The compound melted at 112-13°.

Preparation of 2-Aryl-1-cyano-1-phenylsulphonylethylenes (I, R=CN).—Phenylsulphonylacetonitrile, the aldehyde and ammonium acetate (0.005 *M*, each) in ethanol (10 c.c.) reacted gradually even in the cold to furnish the unsaturated sulphone. To complete the reaction, the mixture was refluxed for 10 minutes and cooled. The separated crystals were collected and recrystallised from ethanol. The data regarding the compounds obtained are recorded in Table I.

2-Benzoyl-1 : 3-diphenyl-2-phenylsulphonyltrimethylenediamine (III).—ω-Phenylsulphonylacetophenone (13.0 g.) (Tröger and Beck, *J. prakt. Chem.*, 1913, *ii*, **87**, 295) and ammonium acetate (3.85 g.) were dissolved in hot absolute ethanol (75 c.c.) and the solution was mixed with benzaldehyde (5.3 g.) and boiled for 2 minutes. On cooling crystals separated. After letting aside for 24 hours, the mixture was diluted with water (50 c.c.) and the product was filtered off, washing with water and ethanol (10 c.c.). Trituration with light petroleum (b.p. 80°-90°, 150 c.c.) furnished the *diamine* (5 g., 43% based on benzaldehyde) as an insoluble fraction which crystallised as colorless needles from petroleum, m.p. 149-52°. (Found: C, 71.12; H, 5.33. $C_{28}H_{26}O_3N_2S$ requires C, 71.48; H, 5.53 per cent).

The fraction which dissolved in light petroleum, after washing with NaOH solution (5%) to dissolve out any unchanged keto-sulphone, yielded *1-benzoyl-2-phenyl-1-phenylsulphonylethylene* (I : R = COPh, Ar = Ph) (5.2 g., 30%) which crystallised as plates from ethanol, m.p. 137-38°. (Found: C, 72.55; H, 4.89. $C_{21}H_{16}O_3S$ requires C, 72.41; H, 4.60 per cent).

When ω-phenylsulphonylacetophenone was condensed with benzaldehyde and ammonium acetate (0.01 *M*, each) in glacial acetic acid (3 c.c.) by refluxing for 10 minutes, only the sulphonylethylene was obtained in 48% yield; no diamine was formed.

2-Benzoyl-1-m-nitrophenyl-2-phenylsulphonylethylamine (II, Ar=*m*-$O_2N.C_6H_4$).—*m*-Nitrobenzaldehyde (1.51 g.) was added to a boiling solution of ω-phenylsulphonylacetophenone (2.6 g.) and ammonium acetate (0.77 g.) in ethanol (100 c.c.) and the solution was set aside for 3 days. The crystals (2.13 g., 52%) separating were washed with ethanol and crystallised from chloroform, m.p. 146-47°. (Found: C, 61.65; H, 4.19. $C_{21}H_{18}O_5N_2S$ requires C, 61.46; H, 4.39 per cent).

2-Benzoyl-1-p-chlorophenyl-2-phenylsulphonylethylamine (II, Ar=*p*-$Cl.C_6H_4$).—The condensation of ω-phenylsulphonylacetophenone (2.6 g.), *p*-chlorobenzaldhyde (1.4 g.) and ammonium acetate (0.77 g.) in the usual way furnished a product, a part of which dissolved in hot ethanol. The insoluble fraction (2.5 g., 63%) crystallised in fine colorless needles from light petroleum and melted at 167-68.5°. (Found: C, 63.01; H, 4.56. $C_{21}H_{18}O_3NClS$ requires C, 63.08; H, 4.51 per cent).

The fraction, soluble in hot ethanol, yielded 1-*benzoyl*-2-p-*chlorophenyl*-1-*phenylsulphonylethylene* as colorless needles (0.6 g., 16%) from ethanol, m.p. 161.5-63°. (Found : C, 65.63 ; H, 4.20. $C_{21}H_{15}O_3ClS$ requires C, 65.88 ; H, 3.92 per cent).

Preparation of 2-*Aryl*-1-*benzoyl*-1-*phenylsulphonylethylenes* (I, R=COPh).—In general, a mixture of ω-phenylsulphonylacetophenone, the aldehyde and ammonium acetate (0.01 *M*, each) in absolute ethanol (25 c.c.) was heated under reflux for 10 minutes and allowed to stand for 1 to 2 days. The crystals separating were washed with a solution of sodium hydroxide (5%) to dissolve out the unchanged keto-sulphone. Crystallisation of the product from a suitable solvent furnished the analytical sample. In Table I are recorded the details of the compounds prepared.

1 : 1-bis-(*Benzoylphenylsulphonylmethyl*)-*ethane* (IV).—A mixture of ω-phenylsulphonylacetophenone (2.6 g.) and acetaldehyde-ammonia (0.31 g.) in absolute ethanol (20 c. c.) was heated under reflux for 30 minutes. When allowed to stand, crystals began to separate after 2 days. After another 2 days the product was filtered off and washed with a 5% NaOH solution and then with water and ethanol. The product (1.0 g., 37%), after crystallisation from dioxan, softened at 192° and melted at 202-203°. (Found : C, 65.57 ; H, 4.83. $C_{30}H_{26}O_6S_2$ requires C, 65.94 ; H, 4.76 per cent).

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STUDIES IN INDIGOID DYES. PART XVI. THIOINDIGOID DYES DERIVED FROM DIPHENYLMETHANE-4 : 4′-DISULPHONIC ACID

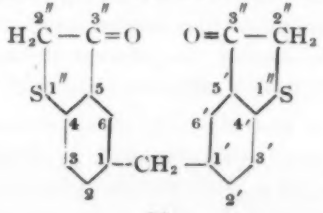
By Paresh Chandra Dutta and Dasrath Mandal

4 : 5-4′ : 5′-Diphenyl-*bis*- (3′-hydroxy-1′-thiophene)-methane (I), prepared from diphenylmethane-4 : 4′-disulphonic acid, has been condensed with various *o*-diketones, and the corresponding *bis*-thioindigoid dyes were obtained with the object of studying colour and its relation to chemical constitution.

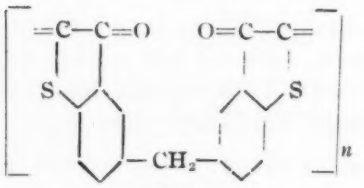
Attempts have been made in this laboratory to prepare *bis*-thioindigoid dyes through *bis*-thioindoxyls with a view to obtaining deeper coloured dyes as compared with the mono-thioindigoids. After having unsuccessful attempts to prepare *bis*-thioindoxyls from diphenyl-4 : 4′-disulphonic acid, and naphthalene-2 : 7-disulphonic acid, as described in Part XIV and Part XV respectively (this *Journal*, 1955, **32**, 339, 427), the attempt to prepare *bis*-thioindoxyl from diphenylmethane-4 : 4′-disulphonic acid has met with success, yielding the expected *bis*-thioindoxyl, 4 : 5-4′ : 5′-diphenyl *bis*-(3′-hydroxy-1′-thiophene)-methane (I). It condenses, as expected, with two molecular quantities of *o*-diketones producing *bis*-thioindigoid dyes, the colour of which, as found, ranges from red to violet. The formation of *bis*-thioindoxyl in this case appears to be due to the methylene bridge present, which has separated the two benzene rings far apart so as to make them two independent units, so that the cyclisation with thioglycollic acid side-chain could take place in both the rings without any hindrance such as the formation of lactone etc., as stated previously (*loc. cit.*).

To obtain the *bis*-thioindoxyl, diphenylmethane-4 : 4′-disulphonic acid (Doer, *Ber.*, 1872, **5**, 796 ; Lapworth, *J. Chem. Soc.*, 1898, **73**, 409), prepared from diphenylmethane, was first converted into disulphochloride and then successively into dimercaptan and dithioglycollic acid ; the latter was cyclised to produce the *bis*-thioindoxyl (I). This indoxyl was then condensed with various *o*-diketones and the corresponding *bis*-thioindigoid dyes (III) obtained. These dyes are insoluble in alcohol, slightly soluble in acetic acid and fairly soluble in nitrobenzene and pyridine. The indoxyl dissolves in dilute caustic soda easily and produces a violet precipitate of the *bis*-indigo (II) by oxidation with potassium ferricyanide. These dyes usually dissolve in alkaline hydrosulphite with a yellow colour and the original dyes are reproduced on oxidation with air. With H_2SO_4 (conc.) the characteristic colour is developed.

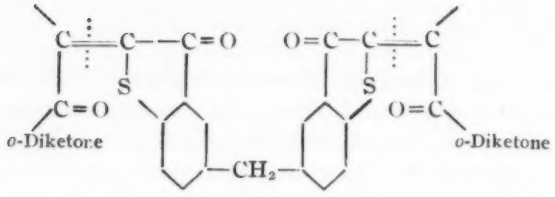
The structures of these compounds may be represented by the following formulae :



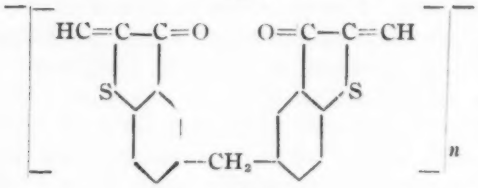
(I)



(II)



(III)



(IV)

As compared with the mono-thioindigoid dyes, these *bis*-thioindigoid dyes are not found to be appreciably deeper in colour as anticipated, and the cause of this may be that the methylene bridge, which has just been the connecting link between two mono-thioindigoid parts, does not exert any chromophoric effect, and so has produced only the colouring effect of the duplication of the monothioindigoid parts.

EXPERIMENTAL

Diphenylmethane-4 : 4′-dithioglycollic acid was prepared by heating diphenylmethane-4 : 4′-disulphochloride (Lapworth, *loc. cit.*) (19 g.) with tin and HCl (conc.) for 20 hours. The residue consisting of excess of tin, dimercaptan and unchanged disulphochloride, after filtration and washing with HCl and water, was warmed with 10% NaOH solution and filtered hot. The yellowish filtrate was mixed with monochloroacetic acid (6 g.), previously neutralised with dilute caustic soda, and warmed on a water-bath for an hour and then filtered from a little precipitate. The filtrate on acidification with HCl gave a voluminous white precipitate of the dithioglycollic acid. This was crystallised from dilute alcohol as colorless shining needles, m. p. 182°, yield 8.7 g. (Found : C, 58.5 ; H, 4.91. $C_{17}H_{16}O_4S_2$ requires C, 58.62 ; H, 4.6 per cent).

4 : 5-4′ : 5′-*Diphenyl*-bis-(3′-*hydroxy*-1′-*thiophene*)-*methane* (I).—Dry, finely powdered dithioglycollic acid (5 g.) was suspended in petroleum ether (50 c. c., b. p. 60°-80°), and to this PCl_5 (7.5 g.) and pyridine (2 drops) were added and the mixture refluxed for an hour, when most of the solid went into solution as the acid chloride.

The clear solution, after removal from a little sticky matter, was allowed to cool in a refrigerator. Gradually a thick oil separated out and collected at the bottom. This oil, after decanting off the petroleum ether, was extracted with fresh petroleum ether three times. The extract (100 c. c.) was then treated with $AlCl_3$ (anhydrous, 5 g.) in portions and the mixture boiled till the evolution of HCl had ceased. After cooling, the petroleum ether was poured out and the molten chocolate complex decomposed by ice and HCl. The substance was thus obtained as a yellow solid, which was filtered and washed with HCl and water. This could not be obtained in a pure condition due to its susceptibility to oxidation. An acetic acid solution of this *bis*-thioindoxyl was used for condensation with various *o*-diketones to obtain the *bis*-thioindigoid dyes. This indoxyl when left exposed to the air became reddish due to oxidation.

bis-(4 : 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*)-*indigo* (II).—The above *bis*-thioindoxyl was dissolved in dilute sodium hydroxide and the greenish filtrate treated with a solution of potassium ferricyanide when the *bis* indigo was obtained as a violet precipitate. This was crystallised from nitrobenzene as a violet crystalline mass, m. p. above 300°. It dissolves in H_2SO_4 (conc.) with a green colour and dyes cotton from yellow hydrosulphite vat in bluish violet shade. [Found : C, 66.05 ; H, 2.8. $-(C_{17}H_8O_2S_2)_n-$ requires C, 66.23 ; H, 2.6 per cent].

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-3 : 3-bis-*indol-indigo*, (IIIa) was prepared by dissolving isatin in acetic acid and adding an acetic acid solution of (I) and boiling the mixture for 15 minutes with the addition of HCl (conc., 0.5 c. c.). The violet-red precipitate, which immediately separated out, was filtered hot and washed with acetic acid and alcohol and crystallised from nitrobenzene as a violet crystalline powder, m. p. above 305°.

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-3 : 3-bis-(5 : 7-*dinitro*)-*indol-indigo* (IIIb) was prepared in the same way as the previous compounds from (I) and 5 : 7-dinitroisatin and crystallised from nitrobenzene as violet needles, m. p. above 310°.

4: 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-3 : 3-bis-(6-*bromo*)-*indol-indigo* (IIIc) was prepared from (I) and *m*-bromoisatin in the same way as described above and crystallised from nitrobenzene as reddish violet crystalline mass, m. p above 300°.

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-2 : 2-bis-*acenaphthylene-indigo* (IIId) was obtained from (I) and acenaphthenequinone, as described above, and crystallised from nitrobenzene as a red crystalline powder, m. p. above 305°.

4:5-4′: 5′-*Diphenyl*-bis-*thiophenomethane*-2 : 2-bis-(5-*or* 6-*nitro*)-*acenaphthylene-indigo* (IIIe) was prepared as above from (I) and 5-nitroacenaphthenequinone and crystallised from nitrobenzene as a pinkish violet crystalline mass, which shrank at 195°, melted at 230°.

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-2 : 2-bis (5 : 6-*dinitro*)-*acenaphthylene-indigo* (IIIf) was prepared from (I) and 5 : 6-dinitroacenaphthenequinone and crystallised from nitrobenzene as a violet crystalline mass, m. p. above 300°.

4:5-4′:5′-*Diphenyl*-bis-*thiophenomethane*-9 : 9-bis-*phenanthrene-indigo* (IIIg) was obtained from (I) and phenanthrenequinone, and crystallised from nitrobenzene as a dark chocolate crystalline mass, m. p. above 300°. It is almost insoluble in alkaline hydrosulphite.

4:5-4′ : 5′-*Diphenyl*-bis-*thiophenomethane*-1 : 1-bis-*aceanthrylene-indigo* (IIIh) was prepared from (I) and aceanthraquinone like the previous compounds, and crystallised from nitrobenzene as a reddish brown crystalline mass, m. p. above 300°.

4 :5-4′:5′-*Diphenyl*-bis-*thiophenomethane*-bis-*ethylene-indigo* (IV) was prepared as a violet precipitate from (I) and glyoxal sodium bisulphite in acetic acid solution by boiling for an hour with HCl (conc., 5 c.c.) and, crystallised from nitrobenzene as a violet crystalline mass, m. p. above 300°. It dyes cotton in pinkish violet shade.

Colour of the solution in H_2SO_4 (conc.) and dyeing shade on cotton of the above compounds and analytical data are shown in Table I.

TABLE I

Compound No.	Colour of soln. in conc. H_2SO_4.	Dyeing shade on cotton.	Mol. formula.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
(IIIa)	Brownish violet	Pink	$C_{33}H_{18}O_4N_2S_2$	69.70	69.47	3.31	3.15
(IIIb)	Green	Chocolate violet	$C_{33}H_{14}O_{12}N_6S_2$		(Nitrogen)*		
(IIIc)	Dirty green	Pink	$C_{33}H_{16}O_4N_2S_2Br_2$	54.18	54.39	2.41	2.2
(IIId)	Green	Do	$C_{41}H_{26}O_4S_2$	76.60	76.87	3.32	3.12
(IIIe)	Do	Bluish green	$C_{41}H_{18}O_8N_2S_2$	67.23	67.40	2.52	2.46
(IIIf)	Greenish brown	Violet	$C_{41}H_{16}O_{12}N_4S_2$	59.73	60.0	2.01	1.95
(IIIg)	Brown	—	$C_{45}H_{24}O_4S_2$	77.85	78.03	3.53	3.46
(IIIh)	Yellowish green	Light copper-red	$C_{49}H_{24}O_4S_2$	79.36	79.46	3.32	3.24
(IV)	Brown	Pinkish violet	$-(C_{19}H_{10}O_2S_2)_n-$	68.02	68.26	3.14	3.0

*Found : N. 11.23; Calc. N, 11.20.

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STUDIES ON THE PERMEABILITY OF COBALT, NICKEL AND SILVER FERRICYANIDE MEMBRANES

By Amir Hasan, Wahid U. Malik and Abani K. Bhattacharya

In studying the permeability of the ferricyanide membranes of Co, Ni and Ag to potassium ferricyanide, potassium sulphate and potassium chloride solutions it has been observed that the membranes are permeable to the free electrolytes. The rate of diffusion of salts through the three membranes is in the order : $KCl > K_2SO_4 > K_3Fe(CN)_6$, but in the reverse order of their adsorption.

The permeability of membranes has not been adequately explained by any theory so far. The seive theory by Traube (1867) and the solution theory by Liebig (*Annalen*, 1862, **121**, 78), and experimentally confirmed by Hermoite (*Ann. chim. phys.*, 1855, **43**, 420) and Kahlenberg (Bancroft, "Applied Chemistry", 3rd. Ed., 1932, p. 133), were shown by Bigellow (*J. Amer. Chem. Soc.*, 1907, **29**, 1576, 1675 ; 1909, **31**, 1194) and Bartell (*J. Phys. Chem.*, 1911, **15**, 659; 1912, **16**, 318, 659; *J. Amer. Chem. Soc.*, 1914, **36**, 646; 1916, **38**, 1036) to fail in certain systems.

The negative adsorption theory was the more favoured view advocated by Mathiew (Bancroft, *loc. cit.*) and Nathanson (*Jahr. wis. Bot.*, 1904, **40**, 431). Tinker (*Proc. Roy. Soc.*, 1916, **92A**, 357 ; 1917, **93A**, 268) and Bancroft (*J. Phys. Chem.*, 1917, **21**, 441) showed that sugar was negatively adsorbed by copper ferro- and ferricyanide membranes and explained the impermeability of sugar molecules to these membranes as the result of negative adsorption. Tinker (*loc. cit.*) and Bartell (*loc. cit.*) suggested the precipitated membranes to be consisted of a collection of colloidal particles in which each visible aggregate comprised smaller colloidal particles affording two types of pores, one being those between the aggregates and the other being those penetrating each aggregate. It was, however, not possible to draw any sharp distinction between them. Their view that the best semi-permeable membranes are those with the smallest pores cannot be held as the only criterion for the osmotic effect in the face of their own experimental results.

Bartell and Hocker (*J. Amer. Chem. Soc.*, 1916, **38**, 1029) observed negative osmosis *i.e.*, diffusion of the solvent from the concentrated solution to the weak one. The rational explanation offered by them for such an osmotic effect is that the osmosis is due to the passage of a charged liquid layer along the capillary tube of the membrane under the driving force of a difference of potential acting as it were between the two faces of the membrane.

Weiser (*J. Phys. Chem.*, 1930, **34**, 335, 1826) observed that these membranes were permeable to chloride, sulphate and ferricyanide but not to ferrocyanogen ions and tried to explain these results on the postulate that due to strong adsorption of ferrocyanide ions, the pores of the membrane were clogged by the chains of oriented ferrocyanide molecules extending from a mono-molecular film on the surface throughout the pores of the solution and the ferrocyanide ions under such a condition were irreversibly adsorbed

to saturate the water in the pores with the salt. Summing up all the observations on the relation between permeability and adsorption, he visualised that the membrane would not be permeable either when negative adsorption took place or strong positive adsorption was observed. Therefore, the condition of permeability through the membranes, according to his view, would be governed by the adsorption of the salts between these two limits.

EXPERIMENTAL

Isotonic solutions of $K_3Fe(CN)_6$, K_2SO_4 and KCl with sucrose solution were prepared by plasmolysis. Soxhlet thimbles of standard dimensions obtained from B.T.L. were used for depositing the ferricyanide gel. Care was previously taken to observe that the same volume of liquid pipetted into the thimble gave the same height. An $N/5$-$K_3Fe(CN)_6$ solution was taken inside the thimble and it was immersed in $N/5$ salt solution such that the height inside and outside was the same, and the same length of time was allowed for deposition. Under these experimental conditions, the area of the permeable surface and the thickness of the membrane were assumed to remain constant for all membranes thus prepared. The membranes were soaked for several days in distilled water prior to their use.

The soaked thimbles were then completely drained out of the water from their surface and 3 c.c. of the electrolyte solution was placed inside the membranes. These were then suspended in 150 c.c. sugar solution, isotonic with the electrolyte, and left stoppered for 48 hours to attain equilibrium. Experiments on diffusion were performed in duplicate and the percentage of diffusion was estimated by determining the loss of the electrolyte inside the thimble. The results are summarised in Table I.

TABLE I

K_2SO_4 (g./litre.)							
	Before diffusion	4.168	4.179	4.086	4.056	4.093	4 093
	After ,,	0.969	0.976	1.525	1.510	2.065	2.005
	% Diffusion	76.74	76.62	62.70	62.80	49.5	51 0

Potassium chloride could not be used in the case of silver ferricyanide membrane owing to the likelihood of chemical reactions with Ag of the membrane material.

To ascertain this relationship between permeability of these membranes and their adsorptive capacity, the adsorption of $K_3Fe(CN)_6$, K_2SO_4 and KCl on freshly precipitated nickel, cobalt and silver ferricyanides was studied by the usual method. In the case of $K_3Fe(CN)_6$, the precipitate became peptised by $Fe(CN)_6^{3-}$ and, hence, it was coagulated before estimating the ferricyanide ions (Bhattacharya and Dhar, *Z. anorg. Chem.*, 1933, **213**, 240 ; Gaur and Bhattacharya, this *Journal*, 1950, **27**, 251 ; Weiser, *loc. cit.*). The results on adsorption are recorded in Table II. The maximum adsorption, calculated from the adsorption isotherms, are as follows :

	$K_3Fe(CN)_6$.	K_2SO_4.	KCl.
1. Nickel ferricyanide	0.8285 g./g.	0.090 g./g.	0.0340 g./g.
2. Cobalt ferricyanide	0.320	0.140	0.0186
3. Silver ferricyanide	0.289	0.038	—

TABLE II

Precipitate.	Wt. of the precipitate.	$K_3Fe(CN)_6$.		K_2SO_4.		KCl.	
		Eqm. conc. (g /lit.)	Amt. adsorbed. (g./g.)	Eqm. conc. in (g./lit)	Amt. adsorbed. (g./g.)	Eqm. conc. (g./lit)	Amt. adsorbed. (g./g.)
Ni ferricyanide	(0.3243 g.)	0.240	0.149	0 197	0.053	0.181	0.014
		0.454	0.322	0.406	0.067	0 364	0.022
		0.739	0.478	0 827	0.090	0 549	0.026
		1.513	0.752			0 732	0.034
Co ferricyanide	(0.1215 g)	0.343	0 068	0.331	0.036	0.371	0.010
		0.501	0.090	0.668	0.068	0.743	0.014
		0.820	0.138	1 005	0.089	1.114	0.017
		1.514	0.225	1 342	0.110	1.486	0.019
Ag ferricyanide	(0.4278 g.)	0.070	0.057	0.219	0.018		
		0.251	0.078	0.442	0.027		
		0.418	0.133	0.666	0.334		
		0 626	0.185	1.017	0 038		

The membranes were found completely impermeable to sugar solution. Adsorption studies from cane sugar solution by the freshly precipitated complexes showed negative adsorption, as shown in Table III. Polarimeter readings for 5% and 3% sucrose solutions are $6^{\circ}.42$ and $3^{\circ}.88$ respectively.

TABLE III

Precipitate.	Wt. of the ppt.	Conc. of sucrose in 100 c.c.	Polarimeter reading.	Water adsorbed (g /g.).
Ni ferricyanide	6.88 g.	5.0 %	6.80	0.79
	6.88	3 0	4 18	1.12
Co ferricyanide	8.43	5.0	7.12	1.05
	8.43	3.0	4.28	1.06
Ag ferricyanide	3.31	5 0	6.53	0 62
	3 31	3 0	3.96	0 79

DISCUSSION

In the light of the controversial theories on the permeability of dissolved molecules, through ferro- and ferricyanide membranes, our observations in a summarised form are recorded below.

The cane sugar solution showed negative adsorption with Ni, Co and Ag ferricyanides. In has also been observed that these membranes are impermeable to sugar solution which is in accordance with the theory developed by Bancroft and Tinker (*loc. cit.*).

An extreme case which could not be explained by this theory is the impermeability of ferrocyanide membranes to $Fe(CN)_6^{4-}$ in spite of the high adsorption of ferrocyanogen ions by copper ferrocyanide. According to Weiser (*loc. cit.*) the membrane becomes impermeable to the solute when (1) there is a marked negative adsorption and (2) when there is a positive adsorption sufficiently great to form a chain of oriented molecules saturating the solvent in the pores. In his opinion the degree of permeability of the membranes to the dissolved solute depends on the adsorption values.

Our experimental data on adsorption of $FeCy_6^{3-}$, SO_4^{2-} and Cl^- by nickel ferricyanide membrane show that the amounts of these ions adsorbed per g. are in the ratio $FeCy_6^{3-}$: SO_4^{2-} : Cl^- as 26.0 : 2.7 : 1.0. If no diffusion have taken place, the percentage loss in concentration due to adsorption should have been proportional to the above ratio. But the % loss inside the thimble as observed (vide Table I) is in the ratio 27.7 : 76.7 : 78.9. It is therefore evident that loss in concentration is very much higher when the adsorption is less and *vice versa*, proving thereby that this big fall in concentration for very low adsorption values is mostly due to diffusion. Similar results follow in the case of cobalt and silver ferricyanide membranes. The adsorption ratio is 17.0 ($FeCy_6^{3-}$) : 7.0 (SO_4^{2-}) : 1.0 (Cl^-) as compared against %diffusion 32.1 : 62.70 : 85.97 for cobalt ferricyanide and 7.6 ($FeCy_6^{3-}$) : 1.0 (SO_4^{2-}) against %diffusion 46.4 : 50.25 for silver ferricyanide membrane. Our observations therefore are in agreement with the views of Weiser (*loc. cit.*).

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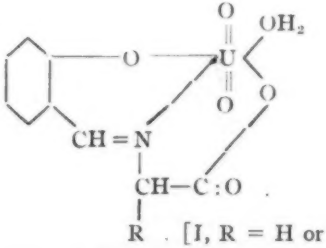
INNER-METALLIC COMPLEX SALTS OF SALICYLALDIMINO ACIDS WITH POLYCYCLIC RINGS. PART II

By Ajit Kumar Mukherjee and Priyadaranjan Rây

Several complex metal chelate compounds of sexivalent uranium and quadrivalent vanadium with salicylaldehyde and amino-acids like glycine, alanine, anthranilic acid and sulphanilic acid have been prepared and their properties studied. Possible structure for the compounds has also been suggested.

In Part I of this series, preparation and properties of a series of polycyclic inner-metallic complexes of copper, nickel, cobalt, manganese and iron with salicylaldehyde and different amino-acids have been reported (Rây and Mukherjee, this *Journal*, 1950, **27**, 707). The configuration of these complexes cannot always be represented by unique and unambiguous structural formulae. The salicylaldehyde molecule in these complexes is believed to undergo condensation with amino-acids giving rise to what may be termed as aldimine-acid, which can function as bidentate or tridentate ligand under suitable conditions. In the present paper several similar polycyclic metal chelate complexes of uranium^{VI} and vanadium^{IV} have been described. Uranium salicylaldehyde itself has also been obtained now in a pure crystalline state, formation of which was previously reported as a result of potentiometric, conductometric and turbidometric titrations involving salicylaldehyde and uranium^{VI} by Bobtelsky and Heitner (*Bull. soc. chim.*, 1952, 358).

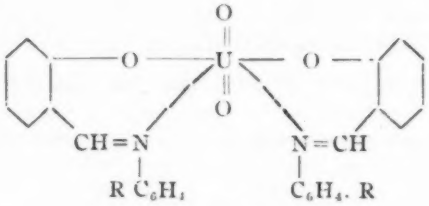
The complex uranyl and vanadyl chelates were all obtained by the interaction of their acetate or chloride, amino-acids and salicylaldehyde in aqueous alcoholic medium. The uranyl compounds could also be prepared from uranyl-salicylaldehyde and the corresponding amino-acids. The glycine and alanine complexes are insoluble or only sparingly soluble in water and dioxan, but freely soluble in alcohol and pyridine. The aldimine-acid molecule in these complexes seems to function as a tridentate ligand. The structure of the complexes can therefore be represented as (I):



[I, R = H or CH_3]

corresponding to that of copper-salicylaldehyde-anthranilate, described in Part I (*loc. cit.*). The uranyl-salicylaldehyde-anthranilic acid and sodium uranyl-salicylaldehyde-sulphanilate, however, behave otherwise and are freeely soluble in water.

The aldimine-acid in these complexes functions as a bidentate ligand with their carboxylic or sulphonic acid group remaining free (II):

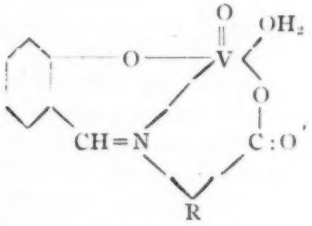


[II, R = COOH or SO_3Na]

All the uranyl compounds are orange-red in colour and are diamagnetic.

The vanadyl complexes are all formed by the condensation of one molecule of the aldimine-acid with one vanadyl radical. The compounds are all similar in their properties and afford moment values lying between 1.78 and 1.81 μ_B corresponding to the spin of one unpaired electron as in the case of simple vanadyl VO^{2+}, ion. The complexes may, however, be regarded as derived from d^2sp^3 octahedral type.

The compound may be represented by the structure (III), corresponding to the uranyl-salicylaldehyde-glycine complex, the oxygen atom of the vanadyl, VO, group, however, here occupying two co-ordination positions:



[III, R = C_6H_4, $-CH_2$ or C_2H_4]

EXPERIMENTAL

Uranyl-salicylaldehyde.—Uranyl chloride (1 *M*) was treated with salicylaldehyde (2 *M*) in hot alcohol. The resulting deep red solution was warmed on the water-bath and to the mixture an alcoholic solution of caustic potash was added dropwise. It was then refluxed on the water-bath for an hour and filtered hot. The filtrate on standing deposited shining red crystals which were filtered, washed with cold water for several times and then recrystallised from hot absolute alcohol. The substance is highly soluble in alcohol, but sparingly soluble in water, dioxan and benzene. It is decomposed by dilute mineral acids. [Found : C, 33.02 ; U, 45.67 ; salicylaldehyde, 46.85. $UO_2(C_7H_5O_2)_2$ requires C, 32.81 ; U, 46.48 ; salicylaldehyde, 47.51 per cent].

Uranium was estimated gravimetrically as U_3O_8 after decomposition of the substance with H_2SO_4 (conc.) and a little HNO_3 (conc.). Salicylaldehyde was estimated as copper salicylaldoxime, as described before. Carbon in the compound was estimated by micro-combustion method.

Uranyl salicylaldehyde-glycine.—Uranyl acetate (1 *M*), salicylaldehyde (2 *M*) and glycine (2 *M*) were refluxed in alcoholic solution on the water-bath till the mixture turned orange-red. This was then filtered ; the filtrate on standing over H_2SO_4 (conc.) deposited shining red crystals.

The same compound could also be obtained by the interaction of uranyl-salicylaldehyde and glycine in hot aqueous alcoholic medium.

The substance is soluble in alcohol and pyridine and practically insoluble in water, acetone and dioxan. It is decomposed by mineral acids and strong alkalies on warming. [Found : N, 3.02 ; U, 49.68 ; salicylaldehyde, 25.20. $UO_2(C_9H_9O_4N)$, H_2O requires N, 2.90 ; U, 49.28 ; salicylaldehyde, 25.26 per cent]. Nitrogen was estimated by Dumas' method (micro).

Uranyl-salicylaldehyde-alanine was prepared like the previous compound using alanine in place of glycine in aqueous alcoholic medium. The filtrate on standing yielded shining orange-red crystals. These were recrystallised from hot ethanol containing a small amount of pyridine. The crystals were dried in vacuo (H_2SO_4).

The compound is soluble in alcohol and pyridine, but sparingly in water and dioxan. It dissolves in dilute alkalies, but is decomposed by mineral acids. [Found : C, 24.28 ; N, 2.83 ; U, 47.88 ; H_2O, 3.62 (by loss at 105°). $UO_2(C_{10}H_{11}O_4N)$, H_2O requires C, 24.14 ; N, 2.82 ; U, 47.88 ; H_2O, 3.68 per cent].

Uranyl-salicylaldehyde-anthranilic acid was prepared like the previous compounds using anthranilic acid (2 *M*) in place of glycine or alanine.

The substance forms shining orange-red crystals, soluble in water, alcohol and pyridine, but only sparingly soluble in acetone and toluene. It is also soluble in dilute alkalies. The aqueous solution is acidic to litmus. [Found : C, 44.11 ; H, 2.78 ; N, 3.70 ; U, 30.79. $UO_2(C_{14}H_{10}O_3N)_2$, H_2O requires C, 43.63 ; H, 2.86 ; N, 3.64 ; U, 30.98 per cent].

Uranyl-salicylaldehyde-sulphanilic Acid (Na-salt).—Uranyl acetate (1 *M*) and salicylaldehyde (2 *M*) were taken in alcohol and warmed on the water-bath ; to the resulting pink coloured solution sulphanilic acid, $NH_2.C_6H_4.SO_3H$, (2 *M*) was added and the mixture made alkaline with caustic soda. This was then refluxed on the water-bath for 2 to 3 hours till a clear solution was obtained. The solution was then filtered hot, and the filtrate on standing deposited orange crystals. These were filtered, washed with cold alcohol, and then recrystallised from hot aqueous alcohol containing a little pyridine. The crystals were dried in vacuum (H_2SO_4).

The substance is highly soluble in water and pyridine, but sparingly soluble in alcohol, dioxan and benzene. Its aqueous solution is slightly alkaline to litmus.

[Found : N, 3.18 ; S, 7.09 ; Na, 4.88 ; U, 26.41 ; H_2O, 4.06 (by loss at 108°). $UO_2(C_{13}H_9O_4NSNa)_2$, 2 H_2O requires N, 3.11 ; S, 7.09 ; Na, 5.10 ; U, 26.38 ; H_2O, 4.07 per cent].

Vanadium-salicylaldehyde-glycine.—Pure vanadyl chloride (1 *M*) and salicylaldehyde (2 *M*) in hot alcohol were treated with glycine (2 *M*) and refluxed on the water-bath for 2 to 3 hours. At the end of the reaction strong alcoholic solution of sodium acetate was added dropwise to the resulting mixture until a clear deep greenish brown solution was obtained. This was then filtered ; the filtrate on standing over H_2SO_4 (conc.) in vacuum yielded dark greenish brown shining crystals. These were filtered, washed with cold water and alcohol, and then recrystallised from hot alcohol containing a little pyridine.

The vanadyl complex is sparingly soluble in water, but fairly soluble in hot alcohol and pyridine. It is, however, less soluble in methyl alcohol and dioxan. The substance dissolves in dilute alkalies, but is decomposed by mineral acids. [Found : N, 5.03 ; V, 18.08 ; salicylaldehyde, 43.68 ; H_2O, 6.45 (by loss at 110°). VO ($C_9H_9O_4N$), H_2O requires N, 5.01 ; V, 18.21 ; salicylaldehyde, 43.57 ; H_2O, 6.42 per cent].

Vanadium was estimated gravimetrically by ignition to vanadium pentoxide after decomposition of the substance with a little concentrated H_2SO_4 and HNO_3.

Vanadium-salicylaldehyde-alanine was prepared like the corresponding glycine compound using alanine in place of glycine. The resulting bright bluish green crystals were recrystallised from hot alcohol containing a little pyridine. It resembles the previous compound in properties. [Found : N, 5.02 ; V, 17.96 ; salicylaldehyde, 43.36. $VO(C_{10}H_{11}O_4N)$, $\frac{1}{2}$ H_2O requires N, 4.91 ; V, 17.88 ; salicylaldehyde, 42.83 per cent].

Vanadium-salicylaldehyde-anthranilate was prepared like the previous compounds. It forms dark greenish blue crystals, soluble in alcohol and pyridine, but only sparingly soluble in water, dioxan and benzene. [Found : N, 4.23 ; V, 14.98. VO ($C_{14}H_{11}O_4N$), $\frac{1}{2}$ H_2O requires N, 4.21 ; V, 15.31 per cent].

Magnetic Measurements.—The magnetic susceptibilities of the compounds were measured in Gouy's balance with a field strength of 9.02×10^3 gauss. The molecular susceptibility was corrected for atomic and ionic diamagnetism. From the corrected susceptibility value for the central metal ion, the value of its magnetic moment was calculated from the relation

$$\mu_B = 2.84 \sqrt{\chi_m \times T}$$

in terms of Bohr magnetons. The results of mesurement at 30.5° are tabulated below.

TABLE I

	Substance.	Colour.	$\chi_g \times 10^{-6}$.	$\chi_M \times 10^{-6}$		μ_B (effective)
				obs.	corr.	
1.	Uranium-salicylaldehyde	Red	−0.1443	...	...	Diamagnetic
2.	Uranium-salicylaldehyde-glycine	Orange-red	−0.2012	...	...	,,
3.	Uranium-salicylaldehyde alanine	Do	−0.1323	...	...	,,
4.	Uranium-salicylaldehyde-anthranilic acid	Do	−0.2018	...	..	,,
5.	Uranium-salicylaldehyde sulphanilic acid (Na)	Do	−0 2482	...	...	,,
6.	Vanadium-salicylaldehyde-glycine	Greenish brown	4.35	1217	1298.6	1.78
7.	Vanadium-salicylaldehyde-alanine	Bluish green	4.26	1214	1302	1.79
8.	Vanadium-salicylaldelyde-anthranilate	Blue	3.76	1251	1328	1.81

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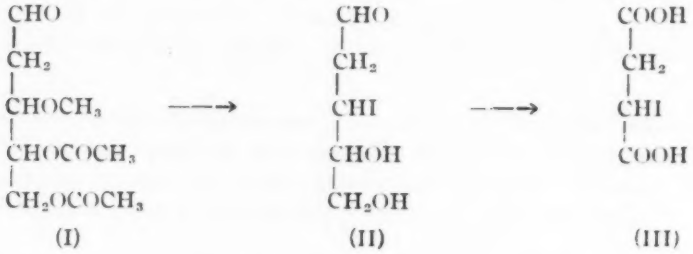
CORCHSULARIN, A NEW BITTER FROM JUTE SEEDS. PART II. 2-DEOXY-*D*-RIBOSE FROM CORCHSULAROSE

By M. A. Khalique and Mofizud-din Ahmed

Corchsularose on demethylation with HI furnished 2-deoxy-3-iodopentose which yielded 2-deoxy-*D*-ribose by alkaline hydrolysis.

Isolation of corchsularin from jute seeds of both the varieties (*Corchorus capsularis* and *C. olitorius*), and its hydrolysis to corchsularose and corchsugenin were reported in the first paper of this series (Khalique and Ahmed, *J. Org. Chem.*, 1954, **19**, 1523). Corchsularose was further shown to be 2-deoxy-3-*O*-methylpentose from oxidative degradation products. Conversion of corchsularose into 2-deoxy-*D*-ribose through its iodo derivative has been reported herein. As corchsularose could not be crystallised, its crystalline diacetate, $C_{10}H_{16}O_6$, was used in this investigation.

Demethylation of corchsularose diacetate (I) with HI afforded a crystalline monoiodo compound ($C_5H_9O_3I$, m. p. 120-21°), which furnished *dl*-iodosuccinic acid (III) when oxidised with chromic anhydride in acetic acid. This reaction, coupled with the fact that corchsularose is 2-deoxy-3-*O*-methylpentose, indicates that the iodine occupies the C-3 position (II).



(I) (II) (III)

Hydrolysis of (II) afforded 2-deoxy-*D*-ribose, identified through its *as*-benzylphenylhydrazone, anilide and acetate derivatives.

Experimental

Isolation of Corchsularose.—Following the methods described in the earlier part (*loc. cit.*) corchsularin was first obtained from jute seeds, then corchsularose and finally corchsularose diacetate in a crystalline from, m. p. 123-24°.

Demethylation of Corchsularose Diacetate.—To corchsularose diacetate (0.4 g.) was added a cold mixture of HI (25 c. c.) and acetic anhydride (15 c. c.) in a Zeisel's flask. The mixture was heated at 130°-140° for 3 hours in an oil-bath while a slow stream of CO_2 was passed through the mixture. After cooling, the mixture was diluted with

about 30 c.c. of water and to it was added a concentrated solution of sodium thiosulphate till the colour was discharged. The clear solution was then extracted with ether. Slow evaporation of ether afforded iodocorchsularose as yellow needle-shaped crystals, which melted at 120-21° after several crystallisations from a mixture of ether and ethanol, yield 0.2 g. (Found: I, 51.76. $C_5H_9O_3I$ requires I, 52.01 per cent). It is readily soluble in methanol, ethanol, ether, acetic acid and pyridine, but sparingly so in water.

Oxidation of the Iodo Compound.—To a solution of the substance in acetic acid (0.5 g. in 40 c. c.) was added slowly at 60° a solution of chromic anhydride in acetic acid (5 g. in 20 c. c.) with constant stirring, heated for an additional hour in a steam-bath and finally evaporated to dryness in a steam-bath. The residue was extracted with ethyl acetate. Crystallisation of the extract from a mixture of ethyl acetate and benzene afforded *dl*-iodosuccinic acid, m.p. 138-40° (decomp.). Westerlund (*Ber.*, 1915, **48**, 1179) records m. p. 135-40° (decomp.). (Found: I, 51.91. Calc. for $C_4H_5O_4I$: I, 52.05 per cent).

Hydrolysis of Iodocorchsularose.—The iodide (0.12 g.) was refluxed with 10% KOH (20 c. c.) for an hour, cooled and extracted with ethyl acetate. On slow evaporation of the solvent an almost white amorphous substance was produced (yield 0.6 g.). This reduced Fehling's and ammonical silver nitrate solutions, restored the colour of the Schiff's reagent, gave a blue Dische colour (*Mikrochem.*, 1930, **8**, 4) and produced a yellow colour with green fluorescence in the Döbner-Miller reaction (Velluz *et al.*, *Bull. soc. chim.*, 1948, 680). These reactions show its deoxy nature and presence of an aldehydic group in the molecule.

Conversion to as-*Benzylphenylhydrazone Derivative.*—To a sample of the amorphous substance (0.06 g.) were added water (4 c. c.) and *as*-benzylphenylhydrazine (0.1 c.c.) and warmed on a hot water-bath to a clear solution, cooled and added more *as*-benzylphenylhydrazine and acetic anhydride (0.2 c.c.). The mixture was heated in a steam-bath for 5 minutes and then ethanol (15 c. c.) was added. On concentration fine needle-shaped crystals of the *as*-benzylphenylhydrazone, m. p. 121-26°, appeared. After charcoal treatment in alcoholic solution, it was further crystallised from ethyl acetate into shining white needles, m. p. 128°, $[\alpha]_D^{30}$ − 17° (in dry pyridine). Levene and Mori (*J. Biol. Chem.*, 1929, **83**, 803) report m. p. 128-30° and $[\alpha]_D^{25}$, −17°.5 (in pyridine)). (Found: C, 68.69; H, 7.03; N, 8.87. Calc. for $C_{18}H_{22}O_3N_2$: C, 68.76; H, 7.05; N, 8.91).

Conversion to 2-*Deoxy*-D-*ribose Anilide.*—The iodide (0.2 g.) was again hydrolysed in the above way with 10% KOH to yield 0.05 g. of an amorphous white substance which was heated under reflux for 4 hours with freshly distilled aniline (0.04 g.) in ethanol (5 c. c.). On cooling, a viscous oily substance was obtained. This gave a yellowish solid substance when triturated with ether. On treatment with activated charcoal in alcoholic solution and crystallisations from a mixture of ethanol-ethyl acetate this gave 2-deoxy-*D*-ribose anilide, m.p. 167-68°, yield 0.07 g. Deriaz *et al.* (*J. Chem. Soc.*, 1949 1879) report m.p. 168°.

Another portion of the amorphous substance, prepared from corchsularose iodide by the above method, was converted into the *acetate of* 2-*deoxy*-D-*ribose* by the conventional pyridine method. The acetate was obtained as a syrup. $[\alpha]_D^{27}, -52°.2$ (in chloroform). Davoll and Lythgoe (*ibid.*, 1949, 2526) report $[\alpha]_D^{17}$, $-52.5°$ in chloroform.

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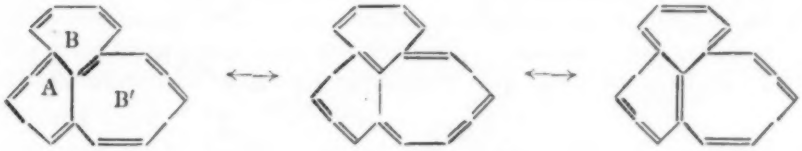
AZULENE AND RELATED SUBSTANCES. PART VIII. 1:8-TETRAMETHYLENE-AZULENE *

By Sukh Dev

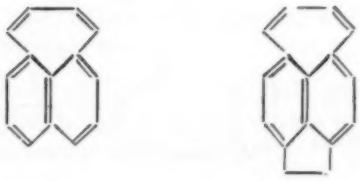
As a preliminary to the preparation of hydrocarbon (I), the synthesis of 1:8-tetramethylene-azulene has been carried out by the diazoacetic ester method.

The fusion of a butadieno chain on to the "peri" (1:8) position of azulene leads to a system (I), which is an analogue of pleiadene (II) (Boekelheide, Langeland and Liu, *J. Amer. Chem. Soc.*, 1951, **73**, 2432; Pullman *et al.*, *J. chim. phys.*, 1952, **49**, 20). The latter hydrocarbon has not as yet been synthesised (cf. Gardner and Horton, *J. Amer. Chem. Soc.*, 1952, **74**, 657), though the closely related acepleiadiene (III) has been recently obtained by Boekelheide *et al.* (*loc. cit.*).

The hydrocarbon (I) is a completely conjugated cyclic polyolefine; the peri angle (123.4°)† of azulene can possibly accommodate a planar seven-membered ring without undue buckling of the molecule. Viewed from the number of π-electrons, it falls into the class of resonating cyclic systems with $(4n+2)$ π-electrons, which according to Hückel (e.g., vide Doering and Detert, *J. Amer. Chem. Soc.*, 1951, **73**, 876; Doereing and Knox, *ibid.*, 1954, **76**, 3203; Sukh Dev, this *Journal*, 1953, **30**, 789; Boekelheide, Langeland and Liu, *loc. cit.*) should possess considerable delocalisation energy. However, the application of this rule to polycyclic systems has been questioned (Roberts *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 4579; Craig, *J. Chem. Soc.*, 1951, 3175). The properties of acepleiadiene reveal that the resonance stabilisation of the peri-ring cannot be very marked, though it is less reactive than ordinary cyclic dienes.



(Ia) (Ib) (Ic)



(II) (III)

* A short communication appeared in *Chem. & Ind.*, 1954, 1021.

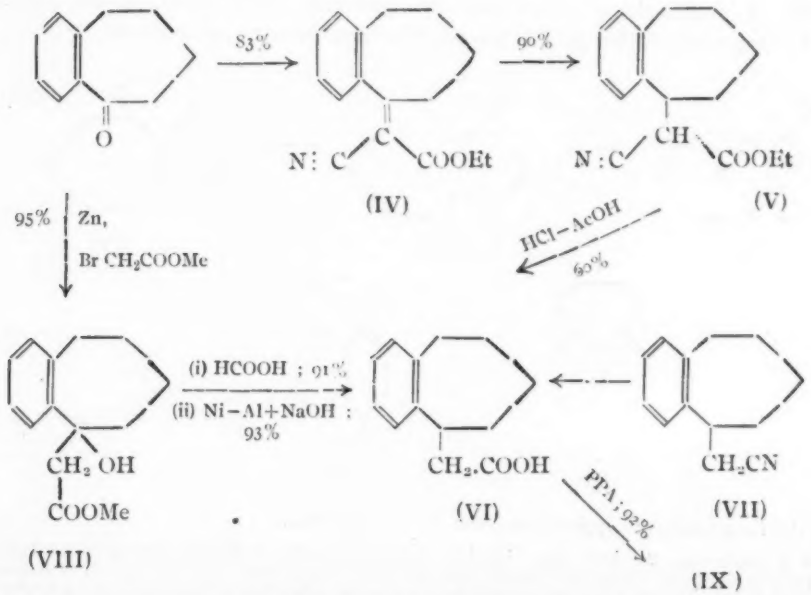
† In a crude way the peri angle has been assumed to be the angle between regular pentagon and (fused) regular heptagon. Azulene is possibly planar (Sklar, *J. Chem. Phys.*, 1937, **5**, 669), however, the C_9-C_{10} bond is known to be appreciably longer than the other bonds (Brown, *Trans. Faraday Soc*, 1948, **44**, 984).

(Ia) and (Ib) may appear to represent two Kekule-like structures of the molecule; however, in (Ia), the molecule is symmetrical about the five-membered ring, either AB or AB′ represents azulene system, which is not the case with (Ib). (Ib) and (Ic) are Kekule-type. The compound can be treated as either a derivative of heptalene or of azulene. But these canonical structures (Ia, Ib, Ic) should impart a partial double bond character to the central bond of azulene (AB or AB′) as well as that of heptalene (BB′). The molecule thus represents an interesting case of non-alternant hydrocarbons.*

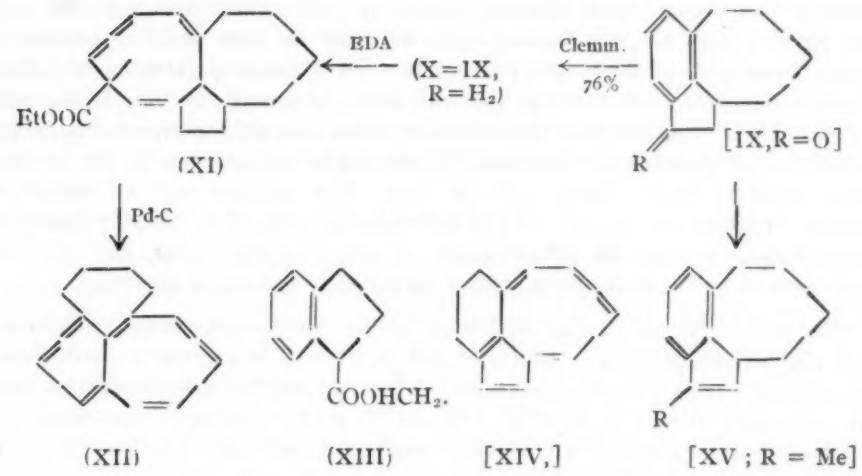
Whereas 1 : 2-benzoazulene shows a bathochromic shift of the longest wave-length of absorption with respect to azulene, the 5 : 6-benzoazulene suffers a hypsochromic shift (Plattner *et al.*, *Helv. Chim. Acta*, 1949, **32**, 2461). The spectra of *cyclo*heptatrieno-azulene (I), which is isomeric with these will be of considerable interest (cf. Pullman and Pullman, *Discussions, Faraday Society*, 1950, **9**, 46; Berthier, Pullman and Baudet, *J. chim. phys.*, 1953, **50**, 209).

As a first step towards the synthesis of (I), its tetrahydro derivative (XII) has been prepared as outlined below.

Benzosuberone was condensed with ethyl cyanoacetate in the presence of benzylamine (Sukh Dev, this *Journal*, 1953, **30**, 443, 665) to yield the ethyl benzo*cyclo*heptylidene-cyanoacetate (IV) in good yield. It was, however, directly subjected to the catalytic reduction to furnish the homogeneous reduced ester (V). Hydrolysis with hydrochloric acid in acetic acid yielded the benzosuberylacetic acid (VI) in 60% yield; from the neutral portion a crystalline material (yield 20%) was isolated, which was identified as the corresponding nitrile (VII).



* It is hoped to present the M.O. calculations of this interesting system in the near future.



(XI) (XII) (XIII) [XIV,] [XV ; R = Me]

A more convenient route for the preparation of (VI) involved the Reformatsky reaction of methyl bromoacetate on benzosuberone (Mentzer, Buu-Hoi and Cagniant, *Bull. soc. chim.*, 1943, **10**, 139 ; Gilmore and Horton, *J. Amer. Chem. Soc.*, 1951, **73**, 1411) to yield the hydroxy-ester (VIII). This was readily dehydrated by 95% formic acid to afford the unsaturated ester. The conversion of this into the acid (VI) is most conveniently accomplished by an adaptation of the general reduction procedure employing Raney nickel-alloy and alkali (Schwenk *et al.*, *J. Org. Chem.*, 1944, **9**, 175). Both hydrogenation and saponification of the unsaturated ester take place simultaneously to furnish the requisite acid in an excellent yield. The procedure (vide Experimental) appears to be quite suitable for the one-step hydrolysis and reduction of the unsaturated esters from the Reformatsky reaction ; thus the indane analogue (XIII) of (VI) can also be similarly obtained in 90% yield (cf. Anderson and Wade, *J. Amer. Chem. Soc.*, 1952, **74**, 2274).

The acid can be readily cyclised to the ketone (IX) A solution of P_2O_5 in phosphoric acid (polyphosphoric acid, PPA) is the reagent of choice for this purpose. This intramolecular acylation has also been carried out by the aluminium chloride as well as by the stannic chloride methods.

The Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) modification of the Wolff-Kishner reduction of (IX) furnished the hydrocarbon in only 60% yield. The Clemmensen reduction proved somewhat better (yield 76%).

The six-membered aromatic ring in (X = IX, R=H_2) was expanded by the Büchner reaction to furnish the *cyclo*heptatriene derivative (XI), expected to be a mixture. This reaction (Braren and Büchner, *Ber.*, 1901, **34**, 982 ; Buchner and Schottenhammer, *ibid.*, 1920, **53**, 865 and various other papers cited there) has been used extensively for the synthesis of various azulenes (e.g., vide Pommer, *Z. angew. Chem.*, 1950, **62**, 281 ; Gordon, *Chem. Rev.*, 1952, **50**, 127) The reaction like the analogous case of ring-

expansion with diazomethane (Doering *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 2305; 1951, **73**, 876; Sukh Dev, this *Journal*, 1953, **30**, 729) is most likely to proceed by a prior decomposition of the ethyl diazoacetate to a diradical [Doering and Knox (Abstracts of papers, 119th Meeting, American Chemical Society, Boston, Mass., April 2, 1951, p. 2M) consider that these divalent carbon intermediates are not free radicals and have termed these species "Carbenes"] followed by its addition to the aromatic system (Badger, *Quart. Rev.*, 1951, **5**, 155). The reaction may be carried out thermally (Büchner *et al.*, *loc. cit.*) or by irradiation with a U.V. lamp* (Schenck and Ziegler, *Naturwiss.*, 1951, **38**, 356; Schenck, *Z. angew. Chem.*, 1952, **64**, 12). Test experiments on indane by the latter method did not show any special advantage.

The ester (XI) on alkaline hydrolysis yielded the corresponding acid mixture, which was dehydrogenated-decarboxylated over 20% Pd—C in a special apparatus (vide Experimental) to afford the required azulene (XII). During this dehydrogenation none of the compound (I) could be detected. Though the crude dehydrogenation product on chromatography furnished a green zone, besides the principal blue band, search for (I) in the green eluterates was fruitless.

The light absorption characteristics of the new azulene are shown in Table I. Plattner and co-workers (e. g., See Haagen-Smit in Zechmeister's "Progress in the Chemistry of Organic Natural Products", 1948, Vol. V, p. 57) have demonstrated that knowing the structure of an azulene and the position of its longest wave-length, spectral band can be calculated with reasonable accuracy. On the basis of these rules the expected spectral shift with respect to that of azulene should be $+21 m\mu$; the 1 : 8-tetramethylene azulene has been treated as an 1 : 8-dialkyl derivative of azulene. The value actually found to be is $+32 m\mu$ (vide Table I); a slightly better agreement is reached if the average $\Delta\lambda$ is compared.

TABLE I

Light absorption of 1 : 8-*tetramethylene-azulene.*

	Visible			Ultraviolet	
No.	$\lambda_{max.}$	ϵ	Spectral shift with respect to azulene.	$\lambda_{max.}$	log ϵ.
1	605 mμ	193	+25	229 mμ	4 20
2	630	174	+26	246	4.28
3	660	159	+27	263	4 23
4	730	58	+32	283	4.39
5			Average +27.5	302	3.84
6				325	3.47
7				350	3.48

* By analogy with the preparation of azulene from indane and diazomethane (Sukh Dev, this *Journal*, 1953, **30**, 729) we had independently arrived at this procedure. Our attention has been drawn to the work of Schenck and Ziegler (*loc. cit.*) through a paper by Sixma and Detilleux (*Rec. trav. chim.*, 1953, **72**, 173). It has also been found that a trace of Cu powder effectively lowers the photochemical decomposition temperature (vide experimental).

The dehydrogenation of the hydrocarbon (X = IX, R = H_2) was investigated in order to see if it could be converted into 1 : 8-trimethylene-azulene (XIV) ; only an orange coloured condensate was obtained. When the vapour phase dehydrogenation was carried out in the presence of tetralin (to act as a hydrogen donor for the reduction of the aromatic ring?), a similar result was obtained. The analogous compound (XV) also did not furnish any blue product under these conditions.

EXPERIMENTAL

All melting and boiling points are uncorrected. All solid samples before analysis (micro) were dried at 75°/1 mm. for several hours.

δ-Phenylvaleric acid was prepared by the method of Cook *et al.* (*J. Chem. Soc.*, 1948, 69). However, the reaction of freshly distilled cinnamaldehyde with malonic acid in anhydrous quinoline was quite vigorous in the initial stages and had to be moderated by occasional cooling in ice ; only five days at room temperature (27°) sufficed for the completion of the reaction. The yield of the pure δ-phenylvaleric acid (b.p. 149°/2 mm., m.p. 57-59°) was 80-82% instead of 64%, as reported by previous authors.

Benzosuberone.—The above acid (60 g.) was cyclised with polyphosphoric acid, prepared from P_2O_5 (360 g.) and orthophosphoric acid (89%, 235 c. c.). The yield of the product was 82%, b.p. 115°/3.2 mm ; $n_D^{29.5}$, 1.5610. (cf. Gilmore and Horton, *loc. cit.*).

The 2 : 4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and was obtained as bright red, lustrous plates from a mixture of benzene and alcohol, m. p. 210.5°. (Found : N, 16.41. $C_{17}H_{16}O_4N_4$ requires N, 16.47 per cent).

Ethyl Benzocycloheptylidene-cyanoacetate (IV).—Benzosuberone (8.0 g., 0.05 *M*) and ethyl cyanoacetate (6.2 g., 0.055 *M*) in benzene (25 c. c.) were condensed in the presence of benzylamine (1.06 g., 0.01 *M*) and glacial acetic acid (3 c. c.) in the usual manner (Sukh Dev, *loc. cit.*). After the separation of water was over (3½ hrs.) the reaction was continued for another one hour, and then cooled, diluted with ether (20 c. c.) and washed first with water (20 c. c. × 2) and then with brine (20 c. c.). From the dried (Na_2SO_4) solution the solvent mixture was removed and the residue fractionated. The product was obtained as a colorless, viscous liquid, b. p. 156°/0.3 mm ; n_D^{29}, 1.5545 ; yield 9.6-10.5 g. (75-82.6%). An analytical sample (central-cut referactionated) had b. p. 160°/0.4 mm ; n_D^{29}, 1.5525 ; d_4^{29}, 1.102 ; M_D, 73.98 (calc. 71.24 ; EM_D. 2.74 ; $E\sum_D$, 1.07). (Found : C, 75.30 ; H, 6.72. $C_{16}H_{17}O_2N$ requires C, 75.29 ; H, 6.66 per cent).

Ethyl Benzocycloheptylcyanoacetate (V).—The freshly distilled unsaturated ester (25.5 g., 0.1 *M*) in ethyl alcohol (40 c. c., distilled over Raney nickel) was reduced in the presence of Adam's platinic oxide (500 mg.). Hydrogenation came to an end after seven hours, when 100.5% of the theoretical amount of hydrogen had been absorbed. The product was worked up to yield 23 g. (89.5%) of a very viscous liquid, b. p. 160°/0.7 mm ; n_D^{28}, 1.5270 ; d_4^{28}, 1.084 ; M_D 72.86 (calc. 71.71). (Found : C, 75.02 ; H, 7.69. $C_{16}H_{19}O_2N$ requires C, 74.70 ; H, 7.39 per cent).

Methyl Benzocycloheptyl-1-oxy-1-acetate (VIII).—This condensation was patterned after the general procedure of Bachmann and Wendler (*J. Amer. Chem. Soc.*, 1946, **68**, 2582). A mixture of benzosuberone (32.0 g, 0.2*M*), activated zinc wool (13.08 g., 0.2 g. atom ; activation of zinc was carried out according to the method of Fieser and Johnson, *ibid.*, 1940, **62**, 575), thiophene-free benzene (50 c. c.), dry ether (50 c. c.) and one-fifth of 0.3 *M* (45.9 g.) of methyl bromoacetate was heated just to boiling and the reaction was initiated by adding a crystal of iodine. When the reaction began (7 min.), the heat source was removed and the rest of the bromo-ester was added dropwise at such a rate that the reaction mixture refluxed gently. This addition required about one hour and most of the zinc had disappeared. When the reaction was thus subsiding, another addition of zinc wool (2 g.) was made and the reaction mixture was heated on the steam-bath for another 2 hours. The product was cooled, treated with glacial acetic acid (25 c. c.) and then diluted with water (50 c. c.) ; the solvent layer was separated after adding some more ether, washed with water (50 c. c.) and then with 2% ammonium hydroxide solution containing some brine (50 c. c. × 5), and after a final washing with brine it was dried (Na_2SO_4). Removal of the solvent from the red solution gave a viscous liquid which on cooling solidified to a crystalline cake, m. p. 50-60°. This was purified by distillation, b.p. 142-43°/0.6 mm., m.p. 61-64°, yield 44.0 g. (94%) (Gilmore and Horton, *loc. cit.*, report 64-65.5° as the m. p. of the recrystallised material). This was used as such in the next step.

Benzocycloheptylacetic Acid (VI) : (i) *From the Reformatsky Product* (VIII).—The above hydroxy-ester (42 g.) was mixed with 95% formic acid (100 c.c.) and heated on the steam-bath for 90 minutes. The somewhat dark reaction mixture was diluted with water (300 c. c.) and the the product extracted with ether (60 c. c. × 3). The combined extracts were washed with water (20 c. c.) and brine (50 c. c. × 2) and dried (Na_2SO_4). The solvent was distilled off from the red solution and the residual unsaturated ester fractionated : b. p. 122°/1 mm ; n_D^{25}, 1.5525 ; yield 35.0 g. (90.4%). An analytical sample had n_D^{25}, 1.5540 ; d^{25}_4, 1.086 ; M_D, 63.71 (calc. 62.25 ; EM_D, 1.46 ; $E\sum_D$, 0.67). (Found : C, 77.90 ; H, 7.56. $C_{14}H_{16}O_2$ requires C, 77.77 ; H, 7.40 per cent).

The above unsaturated ester was reduced and saponified in one operation as follows : To 400 c.c. of water were added pellets of sodium hydroxide (65 g.) in one lot and stirred for a few minutes to effect solution. As soon as dissolved, the unsaturated ester (33 g.) was added ; 5-10 c. c. of alcohol was used to wash in the last traces of the ester. With vigorous stirring (no heating), the Raney nickel (33 g., 40 mesh) was then added in small lots during 2 hours (there should not be much foaming, the second addition of the alloy was made only after the brisk reaction due to the previous lot had subsided). Finally, the reaction mixture was heated (90°-95°) and stirred for another 4 hours, and, after cooling, diluted with water (200 c. c.). The residual nickel (pyrophoric) was removed by filtration and was washed with water (20 c. c. × 5). The combined filtrate and washings were cautiously introduced portionwise, with mixing, into warm dilute sulphuric acid (C. P. H_2SO_4, 140 c. c.

+ water 200 c. c.). After leaving overnight the product was collected, suspended in hot water (20 c. c.) and heated to boiling to remove occluded salts. On cooling, the product was collected, sucked dry and the wet material transferred to a Claisen flask (50 c. c.) along with some CCl_4; this was distilled off, later under suction (water-pump) to remove the moisture. Finally the product was distilled off to afford a colorless viscous liquid, b. p. 155°/0.6 mm., m. p. 98-100°, yield 28 g. (93%). On recrystallisation from a mixture of acetic acid (140 c. c.) and water (140 c. c.) the required acid (VI) was obtained as white, small needles, m. p. 99-101°, yield 27 g. Gilmore and Horton (*loc. cit.*) report the m. p. as 100.5-101° with softening at 99°.

(*ii*) *From Ethyl Benzosuberylcyanoacetate* (V).—A mixture of the cyano-ester (23 g.), HCl (C.P., 115 c.c.) and glacial acetic acid (23 c.c.) was refluxed for 18 hours. Some more HCl (50 c.c.) was added and the refluxing continued for another 20 hours. Most of the volatile acids were then removed by vacuum distillation (water-pump) and the cooled residue treated with warm Na_2CO_3 solution (15%). The neutral portion was taken up in ether and the aqueous alkaline solution after treatment with norit was acidified to yield the crude acid. This was purified by distillation as described above; yield 11 g. after crystallisation from dilute acetic acid, m.p. 99-101° (mixed m.p. with the above material was the same).

Removal of the solvent from the neutral part yielded a crystalline mass (4.5 g). This was recrystallised twice from a mixture of benzene and petroleum ether to furnish white felted needles (2.0 g.), m.p. 67-68°. (Found: C, 84.0; H, 8.2; N, 7.8. $C_{13}H_{15}N$ requires C, 84.3; H, 8.1; N, 7.6 per cent).

This neutral material (50 mg.) was refluxed for 24 hours with aqueous potassium hydroxide (400 mg. in 3 c.c. of water). Some unhydrolysed material was still there. Working up in the usual manner gave an acid (20 mg.), m.p. 98-99°; mixed m.p. with the acid (VI) was 98-101°.

3:4-*Tetramethylene-indanone*-1 (IX, R=O):(*i*) *Polyphosphoric Acid Cyclisation.*—A solution of P_2O_5 (91.8 g.) in syrupy phosphoric acid (89%, 54 c.c.) was prepared in the usual manner. To this benzosuberylacetic acid (10.2 g., 0.05 *M*) was added in one lot. This was cautiously warmed (silica-gel guard tube) by swirling over a free flame till all the acid just melted and a light orange-coloured solution was obtained. This was heated with occasional swirling on the steam-bath for 3 hours. The deep red reaction mixture was poured on to cracked ice (400 g.) and left overnight for the complex to decompose. The crude ketone was collected by filtration, washed with water and digested for a short while with Na_2CO_3 solution (5%, 100 c.c.) to remove any free acid (acidification of the alkaline extract gave 0.3 g. of the crude starting material). The product was filtered, washed with water and dried, m.p. 120-23°, yield 8-8.5 g. (86-92%). The ketone was best purified by distillation from a flask suitable for the distillation of solids (recovery above 95%, b.p. 140°/1 mm., m.p. 122-24°), but the undistilled ketone was pure enough for the next step.

A sample was recrystallised from a mixture of benzene and petroleum ether to furnish white prismatic needles (m.p. 124°; constant). This was next sublimed at 0.5 mm. for analysis. (Found: C, 83.87; H, 7.38. $C_{13}H_{14}O$ requires C, 83.87; H, 7.52 per cent).

The 2: 4-*dinitrophenylhydrazone* was prepared by the usual method (H_2SO_4 method). Crystallisation from benzene gave bright red, fine needles, m.p. 242°. (Found: N, 15.30. $C_{19}H_{18}O_4N$ requires N, 15.30 per cent).

(*ii*) *Ring-closure by the Stannic Chloride Method.*—The acid (10.2 g., 0.05 *M*), covered with thiophene-free benzene (50 c. c.) and with cooling in ice-water, was treated with PCl_5 (10.8 g., 0.052 *M*) in one lot. After 5 minutes in the ice-bath and 20 minutes at room temperature (25°), the reaction mixture was heated at 65°-75° till all the PCl_5 had disappeared (10 minutes). This was cooled in an ice-salt bath and stannic chloride (28.7 g., 0.11 *M* ; 13 c.c.) was introduced in one lot. After swirling in the ice-bath for a few minutes it was allowed to warm up to room temperature. After 3½ hours at room temperature the dark red reaction mixture was poured into ice and HCl (35 c.c.). The benzene layer was separated and the aqueous part extracted once with the same solvent (25 c.c.). The combined extracts were washed successively with HCl (10%, 25 c.c.), water (30 c.c.), Na_2CO_3 in brine (30 c.c.) and finally with brine (30 c.c.). The dried solution (Na_2SO_4) was concentrated to *ca.* 20- 25 c.c. and diluted with petroleum ether (30 c.c.); after about an hour another 50 c.c. of petroleum ether was added and after several hours at 0°, the product was collected as light brownish prismatic needles, m.p. 119-20°, yield 7.7 g (82.8%).

(*iii*) *By the Aluminium Chloride Method.*—The acid chloride was prepared as above from the same amounts of the acid and PCl_5. $POCl_3$ and benzene were removed under suction at 80°. The residue was treated with benzene (20 c.c.) which was also distilled off as above. This operation was repeated twice more. The cooled residue was taken up in dry thiophene-free benzene (50 c.c.). This was cooled in ice and treated with $AlCl_3$ (7.98 g., 0 059 *M*; freshly powdered) in one lot. After five minutes' swirling in the ice-bath, the reaction was allowed to proceed at room temperature. When it had slackened (½ hr.) it was warmed at 70°-80° till all the $AlCl_3$ had just disappeared (½ hr.). The cooled reaction mixture was worked up as above; yield of the product of m.p. 120-23° was 8.0 g. (86.0%).

1:7-*Tetramethylene-indane* (X = IX, R = H_2).—Zinc wool (50 g.) was amalgamated with mercuric chloride (5.0 g.) in the usual manner and covered with water (30 c.c.), HCl (70 c.c.) and toluene (60 c.c.). To this the above ketone (18.6 g., 0.1 *M*) and glacial acetic acid (2 c.c.) were added. The mixture was refluxed for 34 hours; during this period HCl (120 c.c.) was added in portions at suitable intervals. The toluene layer was washed over with water and the yellow solution dried (Na_2SO_4). About two-thirds of the solvent were distilled off and the residue passed down a column of activated silica-gel (-40 mesh; 13 cm. × 2 cm.). The column was washed with petroleum ether (100 c.c.). From the combined eluterates the solvent was flashed off and the residue fractionated to afford the required hydrocarbon as a colorless, mobile liquid, b.p. 120°/6 mm ; n_D^{28}, 1.5575; yield 13.0 g. (75.5%). (Found: C, 89.92 ; H, 9.34. Calc. for $C_{13}H_{16}$: C, 90.69 ; H, 9.30 per cent). Von Braun and Roth (*Ber.*, 1927, **60**, 1182) give 127-28°/12 mm. as the boiling point.

When reduction of the ketone (1.86 g.) was carried out with hydrazine hydrate (85% ; 1.47 g., 0.025 *M*) in glycol (15 c.c.) containing KOH (1.85 g., 0.033 *M*) by the general procedure of Huang-Minlon (*loc.cit.*), the yield of the indane was only 60%.

Ring-expansion Experiments

(*i*) *Büchner Reaction on Indane.*—Indane (17.7 g., 0.15 *M*) along with copper powder (5 mg.) was placed in a quartz flask carrying a thermometer dipping into the liquid, and a dropping funnel. This was directly illuminated with a mercury-arc lamp; the distance was so adjusted that the thermometer registered a temperature of 90°-100°. Ethyl diazoacetate (EDA ; 3.4 g., 0.03 *M*) was best prepared by the method of Smith and McKenzie (*J. Org. Chem.*, 1950, **15**, 74), and it was then added during 5 hours; evolution of nitrogen was quite smooth. Irradiation was continued for another 5 hours to complete the decomposition of EDA. The product was then fractionated off to yield the required product, b.p. 110-15°/1 mm ; n_D^{30}, 1.5070; yield 1.5 g. (24.3% based on EDA). Hippchen (Fiat Report No. 10.33, Jan. 14, 1947) reports b.p. 122-124°/1.5 mm ; n_D^{20}, 1.524.

When the condensation of EDA with indane was carried out thermally by a procedure described below, the yield was 2.5 g. (40% based on EDA).

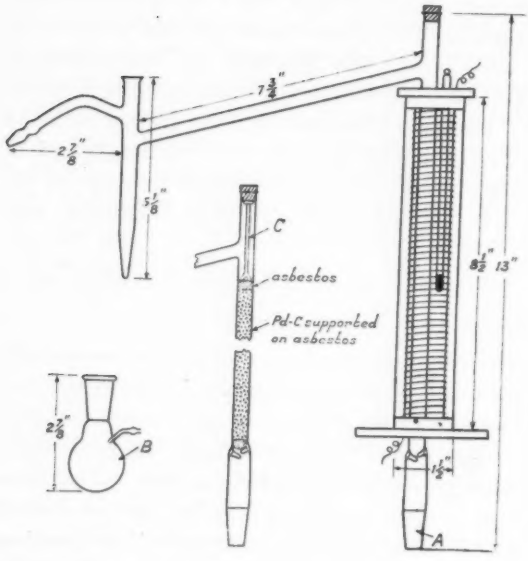
(*ii*) *Ring-enlargement of* 1: 7-*Tetramethylene-indane* (X).—The hydrocarbon (X, 12.0 g, 0.07 *M*) was heated to 130°-140° in a modified Claisen flask in the presence of small pieces of pumice stone (*ca.* 2 g., this appears to help in the smooth evolution of N_2). EDA (4 c.c.) was then added during 6 hours. After the addition the temperature was raised to 160°-165° and maintained there for another one hour. Fractionation yielded a fore-run of the unreacted hydrocarbon (10.5 g.) and the desired product was collected at 150°-170°/1 mm. as a red oil (3.0 g.). The recovered hydrocarbon was treated with EDA (4 c.c.) as before. This operation was carried out for five times in all to finally yield a total of 9.4 g. of the condensation product and 2.8 g. of the unchanged hydrocarbon (purified by chromatography over silica gel ; b.p. 96-97°/1 mm.). The condensation product was carefully refractionated (9"-Vigreux column with a total condensation variable take-off-type still-head) to obtain the desired compound (XI) as a reddish oil, b.p. 170-75°/2 mm., yield 6.6 g. (Found : C, 79.0; H, 8.7 $C_{17}H_{22}O_2$ requires C, 79.0; H, 8.5 per cent).

The above ester (6.5 g.) was hydrolysed by refluxing for 10 hours with KOH (5.0 g. + 10 c.c. of water) in alcohol (50 c.c.). The alkaline solution was diluted with water (150 c.c.) and extracted with ether to remove the neutral material (0.5 g). Acidification with HCl (conc.) to p_H 2 liberated the acid which was taken up in ether (25 c.c. × 3). Working up in the usual manner gave the acid as a dark red, highly viscous liquid, b.p. 195°-200°/1 mm., yield 4.5 g. (77%). An analytical sample was prepared by evaporative distillation ("Kügel Rohr") at 140°/7 × 10^{-3} mm. (Found : C, 78.2; H, 7.3. $C_{15}H_{18}O_2$ requires C, 78.2; H, 7.8 per cent).

1 : 8-*Tetramethylene-azulene* (XII).—A special apparatus (Fig. 1) was devised for the dehydrogenation -decarboxylation of the above derivative of *cyclo*heptatriene-carboxylic acid. The apparatus appears to be useful for the vapour-phase dehydrogenation of solids or viscous liquids. In this apparatus, the material is slowly distilled through a bed of the hot catalyst, under vacuum.

The catalyst-bed was packed with 20% Pd—C (0.5 g., Org. Syntheses, Vol. 26, p. 78, procedure D) mixed with freshly ignited asbestos (medium size ; 1 g.) ; two plugs (1 cm. each) of asbestos were placed at either end to keep the packing in place. At the top of the upper asbestos plug, a fork-shaped piece (C) was placed ; this was held in between the plug and the cork ; this helped to keep the packing in place during the dehydrogenation. The flask (B) containing the above acid (3.0 g.) was attached at A and the apparatus was very slowly evacuated to a pressure of *ca.* 35-40 mm ; dry nitrogen was then very gently let in so that the mercury in the manometer was slightly depressed. The furnace was slowly heated (one hour) to 320°-340° and was maintained there for another ½ hour to activate the catalyst ; any moisture which might have condensed in the receiver was removed by gently warming it. The receiver was next cooled in a freezing mixture and the acid slowly distilled with a free flame through the hot bed of the catalyst during half-an hour. The deep blue (towards the end, green) distillate was taken up in petroleum ether (10 c. c.) and chromatographed over alumina (Activity I/ basic ; 18 cm. × 1.8 cm.). The column was washed with petroleum ether (60 c. c.) and later with a mixture of petroleum ether (4 parts) and ether (1 part) till the blue band was eluted out, this being collected separately (*ca.* 60 c. c.). A green band was left on the column which was washed out with ether (20 c.c.).

FIG. 1



Removal of the solvent from the blue fraction yielded a deep blue, thick oil (300 mg., 12.5%) which soon became semi-crystalline. To this trinitrobenzene (250 mg.), dissolved in hot alcohol (8 c. c.), was added, heated to boiling and allowed to crystallise, first at room temperature (22°) later at 5° (one hour). The product was collected and washed with ice-cold alcohol (2 c. c.), yield 240 mg., m. p. 130-32°. Two recrystallisations from alcohol (4 c. c.) gave black needles of the *tirinitrobenzene complex*, melting constantly at 137-39° (yield 140 mg.). (Found : C, 60.6 ; H, 4.5 ; N, 10.59. $C_{20}H_{17}O_6N$ requires C, 60.75 ; H, 4.3 ; N, 10.62 per cent).

The green fraction on being rechromatographed (Al_2O_3 ; 12 cm. × 1 cm.) and developing with a mixture of 20 parts of petroleum ether and one part of benzene, could be separated into three zones, the upper most being the green one, followed by a yellow

and a blue band. It was suspected that the green zone might contain the compound (I), but it had not been possible to prepare any derivative from this so far.

Pure 1 : 8-*tetramethylene-azulene* was isolated by passing a solution of its trinitrobenzene complex (100 mg.) in the smallest amount of benzene and diluted with petroleum ether (5 c. c.) through a column of alumina (15 cm. × 1.4 cm.); the blue band was eluted out by washing it with petroleum ether (4 parts) containing ether (1 part). Removal of the solvent at 100° furnished the azulene as blue plates, m. p. 47-48°, yield 30 mg. (Found : C, 92.2; H, 7.7. $C_{14}H_{14}$ requires C, 92.3; H, 7.7 per cent).

The *spectra* were measured on a Beckman DU spectrophotometer using a solution of the azulene in 95% ethanol. In the ultraviolet region readings were taken at intervals of 2 mμ, at turning points at intervals of 1 mμ, while the visible range was scanned at 5 mμ intervals, at turning points 2.5 mμ.

1-*Methyl*-3 : 4 *tetramethylene-indene* (XV).—To a solution of methylmagnesium iodide (from methyl iodide 2.8 g., Mg, 0.29 g. and ether, 20 c. c.) was added a solution of the indanone (IX, R=O; 1.86 g.) in dry S-free benzene (20 c.c.). This was refluxed for 3 hours and the clear yellowish solution deposited a crystalline complex on cooling. On decomposition with ice and HCl and working up in the usual manner, the crude carbinol was obtained. This was dehydrated by treatment with formic acid (90-95% ; 10 c. c.) for 2 hours on the steam-bath. Dilution with water and working up with petroleum ether, followed by distillation, yielded the required hydrocarbon as a colorless liquid, b. p. 109°/1 mm., m. p. 51-53°, yield 0.7 g. (Found : C, 90.89 ; H, 8.72. $C_{14}H_{16}$ requires C, 91.30 ; H, 8.69 per cent).

A *trinitrobenzene complex* could be prepared from an alcoholic solution in yellow needles, m. p. 87-90° (melt cleared at 100°). (Found : N, 10.62. $C_{20}H_{19}O_6N_3$ requires N, 10.58 per cent).

1-*Indanylacetic Acid* (XIII).—A Reformatsky reaction with ethyl bromoacetate (50.1 g., 0.3 *M*) was carried on 1-indanone (26.4 g., 0.2 *M*) using activated zinc wool (13.08 g., 0.2 g. atom). The procedure was the same as outlined above for benzosuberone. After the addition of the bromo-ester, which required one hour, the reaction mixture was refluxed for another 3 hours and worked up with glacial acetic acid (20 c. c.). This afforded the ethyl 1-indanylidene-acetate directly, b. p. 135°-145°/3 mm., yield 30 g. (75%) (cf. Braun, Danziger and Kohler, *Ber.*, 1917, **50**, 56 ; Anderson and Wade, *loc. cit.*).

The above unsaturated ester (28 g.) was simultaneously reduced and saponified by Raney nickel alloy (25 g.) and NaOH (55 g. in 400 c. c. of water) by the procedure described above for the preparation of benzosuberylacetic acid. The product was purified by distillation, b. p. 144-48°/0.7 mm. The colorless, viscous distillate crystallised out during distillation, m. p. 59-60°, yield 21 g. (90%). Recrystallisation from acetic

acid (63 c. c.) and water (84 c.c.) gave colorless flat needles, m. p. 60-61° (20 g.). Anderson and Wade (*loc. cit.*) give m. p. 59-60°, while Braun *et al.* (*loc. cit.*) report 60-61° as the m. p.

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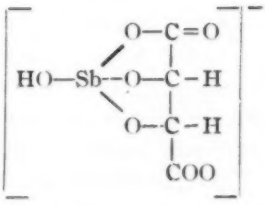
REACTION OF TARTAR EMETIC WITH ALKALI

By Ch. B. Nanda and S. Pani

Sodium hydroxide is quantitatively neutralised by a solution of tartar emetic and 1 g. atom of antimony is removed from the solution as hydrated oxide by 1 g. equivalent of alkali. Hydrated antimony oxide, the product of hydrolysis of antimonyl tartarate ion (vide this *Journal*, 1955, 32, 165) is either directly formed or formed from antimonyl ion by a second reaction. The co-ordination number of antimony in the first product of the reaction would most probably be four. It is proposed that antimonyl ion and hydrated antimonious oxide (antimonious acid) which are interconvertible and present in aqueous solution, are $\left[\begin{matrix}Sb(OH)_2\\(OH_2)_2\end{matrix}\right]^+$ and $\left[\begin{matrix}Sb(OH)_3\\OH_2\end{matrix}\right]$ respectively and supported by other evidences.

It has been observed that the solubility of antimony oxide in tartaric acid first increases with increasing amount of neutralisation of tartaric acid. The solubility is, however, maximum in 50% neutralised solution and rapidly decreases with further neutralisation. It is peculiar to note that similar type of solubilities has been observed in all other systems studied by S. Pani (one of the authors) and others with oxalic, lactic, glycollic, citric acid etc. Besides, a citrate and a gluconate complex of antimony in which the ligands occupy three co-ordination positions and the fourth position occupied by a molecule of water as in antimonyl tartrate ion (Samantara, Rao and Pani, this *Journal*, 1955, **32**, 165, 197; Reihlen and Hezel, *Annalen*, 1931, **487**, 213) have been reported. Further, the dissociation of the aquo-complexes like acids into hydrogen ion and the corresponding hydroxo-complex has also been reported (Das and Pani, this *issue*, p. 537; Patra and Pani, unpublished). A similar hydroxo-complex with tartrate ligand has not been reported by Samantara, Rao and Pani (*loc. cit.*). The following work was undertaken to investigate the existence of the hydroxo-complex



and the reactions leading to the decrease in antimony content of the solution when more than 50% neutralised tartaric acid was used as the solvent.

Experimental

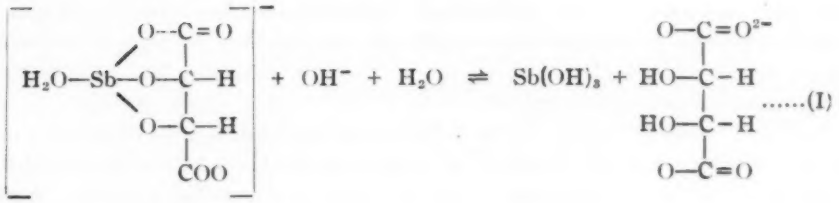
The chemicals used were of Analar quality. Approximately 0.15 *M* solution of tartar emetic was prepared and the solution was standardised against standard potas-

sium bromate solution. A known volume of the solution was taken in a 250 c.c. measuring flask and calculated amounts of a standard sodium hydroxide solution (standardised against standard succinic acid) were added. In each set of experiments the proportion of g. moles tartar emetic to g. equivalent of alkali was kept constant (10 : 1, 6 : 1, 5 : 1 and 4 : 1). There was a precipitate in each case. The mixtures were diluted to 250 c.c., neglecting the volume of the precipitate, and allowed to stand for one day. The mixtures were then transferred to dry stoppered bottles and shaken electrically for 3 to 4 days and then kept in an air thermostat at 35° for 2 to 3 days till equilibrium was established. The antimony contents of the solution (filtrate) were determined by standard potassium bromate and p_H was measured by a Marconi p_H meter. The results are recorded in Table I.

TABLE I

$[E]_a$	[Sb].	p_H.	$[T^{2-}]\times10^3$.	$K\times10^{-7}$.	[E]	[Sb].	p_H.	$[T^{2-}]\times10^3$	$K\times10^{-7}$.
		Series 10 : 1.					Series 6 : 1.		
0.12443	0.11342	5.84	1.088	1.386	0 08963	0 07480	5.99	1.469	2.013
0.11060	0.10068	5.82	0.9788	1.471	0.07988	0.06640	5 98	1 335	2.106
0.09678	0.08794	5.80	0.8718	1.571	0.06989	0.05820	5.97	1.158	2 133
0.08295	0.07581	5.78	0.7473	1.635	0.05991	0.04980	5.94	1.001	2 308
0.06913	0.06307	5.74	0.5969	1.721	0.04993	0 04140	5.90	0.843	2.565
0.04148	0.03791	5.68	0.3506	1 931	0.02996	0.02500	5 80	0 489	3.101
		Series 5 : 1.					Series 4 : 1.		
0.12443	0.09995	6.18	2.439	1 613	0.08963	0.06760	6.20	2.204	2 05
0.11060	0.08879	6.16	2.168	1.684	0.07988	0.06020	6.18	1.964	2.16
0.09678	0.07675	6.12	1.990	1.964	0.06989	0.05260	6.13	1 726	2.43
0.08295	0.06672	6.08	1.611	2.013	0.05991	0.04500	6.10	1.491	2.63
0.06913	0.05555	6.02	1.347	2 309	0.04993	0 03740	6.03	1.252	3 13
0.04148	0.03324	5.96	0.816	2 820	0 02596	0.02240	5.96	0 756	3.70

The alkali added is one tenth to one fourth of the concentration of tartar emetic but the change in p_H is comparatively very small and the concentration of hydrogen ion can be taken as constant. The alkali added is therefore quantitatively utilised by the reaction. It is further noted that the g. atom of antimony removed from the solution is equal to g. equivalent of sodium hydroxide added (the difference is very small and within the limits of experimental error). The precipitates obtained were dried at 110°-120° and analysed for antimony content (in some cases) and was found to be pure antimony oxide. The precipitate is therefore hydrated antimony oxide. The reaction can be represented by equation (I) and the equilibrium constant K_1 is given by equation (I-1) where [Sb], $[OH^-]$ and $[T^{2-}]$ represent the molar concentrations of the complex, hydroxyl ion and tartrate ion respectively.

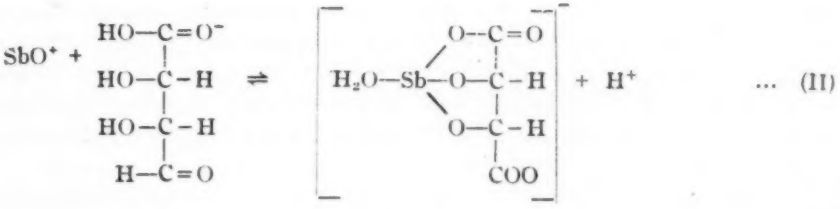


(I)

$$\frac{[T^{2-}]}{[Sb] \times [OH]^-} = K_1 \qquad \ldots \quad (I\text{—}1)$$

The solubility of antimony oxide in water being very small, the whole of the antimony in the solution is taken as the complex. The free tartrate [T] is obtained by subtracting [Sb] from the total tartar emetic originally taken (per litre of solution), (E). The concentration of tartrate ion, $[T^{2-}]$, is calculated from the free tartrate, the p_H of the solution and dissociation constants of tartaric acid [the first and second dissociation constants of tartaric acid are taken to be 0.331×10^{-3} and 1.45×10^{-4} (Clark "Hydrogen ions" 3rd Ed.)].

The calculated values of K_1, shown in Table I, are fairly constants. The total antimony in the solution being present as antimonyl tartrate complex (I), the reaction represented by the equation (II) should also be in a state of equilibrium (Samantara, *et al., loc. cit.*, p. 197). The equilibrium constant K_{II} of the reverse reaction is given by equation (II-1) where $[SbO^+]$, $[HT^-]$ and $[H^+]$ represent the molar concentrations of antimonyl ion, bitartrate ion and hydrogen ion respectively.



$$\frac{[SbO^+] \times [HT^-]}{[Sb] \times [H^+]} = K_{II} \qquad \ldots \quad (II\text{-}1)$$

Substituting $7.7 \times 10^{-18}/[OH^-]$ for $[SbO^+]$ (Gayer and Garrett, *J. Amer. Chem. Soc.*, 1952, **74**, 2353) and $[HT^-]$ by $\left\{\frac{[H^+]}{k_2} \times [T^{2-}]\right\}$ where k_2 is the second dissociation constant of tartaric acid, it can be shown that

$$\frac{k_2}{7.7 \times 10^{-18}} \times K_{II} = K_1 \qquad \ldots \quad (III)$$

K_{II} is also constant. These equilibrium constants therefore simply confirm the equilibrium existing between antimony oxide and antimonyl ion in aqueous solution as reported by Gayer and Garrett (*loc. cit.*). There is, however, no evidence for the hydroxo-complex, as suggested earlier.

The first product formed in the reaction is obtained due to the rupture of the three Sb—O—C bonds in the complex by hydrolysis. It is therefore expected that the co-ordination number of antimony would be four in the initial product. Whether antimonyl ion is first formed and then converted into hydrated antimony oxide or hydrated antimony oxide is directly formed is immaterial since they are inter convertible and they exist in a state of equilibrium in aqueous solution in contact with solid oxide. It is therefore expected that antimonyl ion and the species of hydrated antimony oxide existing in the solution (antimonious acid) would be respectively

$$\left[Sb \begin{matrix} (OH)_2 \\ (OH_2)_2 \end{matrix} \right]^+ \text{ and } \left[Sb \begin{matrix} (OH)_3 \\ OH_2 \end{matrix} \right].$$

The above structure not only explains the ready inter conversion of the two (equation IV)) but also the weak acid character of antimonious acid (equation V).

$$\left[Sb \begin{matrix} (OH)_3 \\ OH_2 \end{matrix} \right] + H^+ \rightleftharpoons \left[Sb \begin{matrix} (OH)_2 \\ (OH_2)_2 \end{matrix} \right]^+ \quad \ldots \text{(IV)}$$

$$\left[Sb \begin{matrix} (OH)_3 \\ OH_2 \end{matrix} \right] \rightleftharpoons H^+ + \left[Sb(OH)_4 \right]^- \quad \ldots \text{(V)}$$

If antimonious acid is represented by HO−Sb=O, the acid would be comparitively a strong one having dissociation constant of the order 10^{-2} (Pauling, "General Chemistry", p. 394), which is actually not.

Besides, the dissociation of HO−Sb=O into a hydroxyl ion and SbO^+ and again to hydrogen ion and SbO_2^- appears to be less probable (W. Huckel, "Structural Chemistry of Inorganic Compounds", Vol. II, p. 924). The above structures are further supported by observation of Britzinger that antimonite ion is $Sb(OH)_4^-$ (FIAT Review of German Science, 1919-1945, Inorganic Chemistry, Vol. 25, Part III, p.8.).

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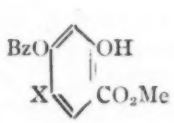
FRIES ISOMERISATION AND FRIEDEL-CRAFTS REACTION WITH 2 :4-DIHYDROXY-5-BROMO(AND 5-CHLORO)-BENZOIC ACIDS AND THEIR METHYL ESTERS

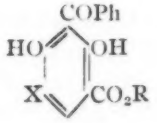
By J. I. Setalvad and N. M. Shah

The Fries isomerisation of benzoyl esters of methyl 2 :4-dihydroxy-5- bromo(& 5-chloro)-benzoate yields methyl 2 :4-dihydroxy-3-benzoyl-5- bromo(& 5- chloro)- benzoate and/or the corresponding keto-acid, depending upon the conditions of the experiments. The Friedel-Crafts benzoylation furnishes also the same ketonic products. The keto-acid on decarboxylation yields 2-benzoyl-4-bromo- (or 4-chloro)- resorcinol, identical with the hydrolysis product of 8-benzoyl-7-hydroxy-6-bromo (or 6-chloro)--4-methylcoumarin.

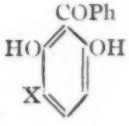
In continuation of our previous work (this *Journal*, 1953, **30**, 373), the Fries isomerisation of benzoyl esters of methyl 2 : 4-dihydroxy-5-bromo-(& 5-chloro-)benzoate and the corresponding free acids has been investigated and the results are described in this communication.



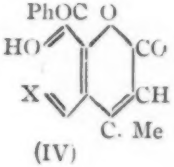
(I)



(II)



(III)



(IV)

Methyl 2-hydroxy-4-benzoyloxy-5-bromo-(or chloro-)benzoate (I, X = Br or Cl) did not isomerise at temperatures lower than 140°. The isomerisation at 150° afforded a mixture of the keto-ester and the keto-acid (II : X = Br or Cl ; R = Me and H), separated by sodium bicarbonate treatment ; at 170° only the keto-acid was obtained in diminished yield, hydrolysis occurring simultaneously with the migration. The above migrations were also successfully carried out in nitrobenzene as the solvent.

Methyl 2 : 4-dihydroxy-5-bromo- (or 5 chloro-)benzoate on Friedel-Crafts' benzoylation furnished methyl 2 : 4-dihydroxy-3-benzoyl-5-bromo-(or 5-chloro-)benzoate (II : X = Br or Cl ; R = Me), identical with the migration products. Very little or no hydrolysis occurred during the Friedel-Crafts benzoylation in contrast to the Fries reaction, the keto-ester (II : X = Br or Cl ; R = Me) being obtained in good yield.

The keto-esters on hydrolysis furnished the corresponding keto-acids (II : X = Br or Cl ; R = H). which were decarboxylated to 2-benzoyl-4-bromo- (or 4-chloro-) resorcinol (III : X = Br or Cl), identical with the hydrolysis product of 8-benzoyl-7-hydroxy-6-bromo(or 6-chloro) -4-methylcoumarin (Setalvad and Shah, this *Journal*, 1954, **31**, 600), and they easily underwent the Pechmann condensation with ethyl acetoacetate producing 8-benzoyl-7-hydroxy-6-bromo(or 6-chloro)-4-methylcoumarin (IV : X = Br or Cl) (*ioc. cit.*).

The Fries migration of the free benzoyloxy-acids could not be carried out as they could not be prepared in a pure condition. The hydroxy-acids, however, underwent Friedel-Crafts' benzoylation affording the same keto-acids (II : X=Br or Cl ; R= H), obtained by hydrolysis of the migration product of the esters.

EXPERIMENTAL

Fries Migration of Methyl 2-Hydroxy-4-benzoyloxy-5-bromobenzoate

Methyl 2-hydroxy-4-benzoyloxy-5-bromobenzoate (I : X=Br) was prepared by heating methyl 2 : 4-dihydroxy-5-bromobenzoate (5 g.) in pyridine (2 c. c.) with benzoyl chloride (5 g.) at 100° for 3 hours. The crude product was treated with sodium bicarbonate solution (5%), and the insoluble residue twice crystallised from acetic acid in colorless needles, m. p. 173°, yield 4 g. (Found : Br, 22.4. $C_{15}H_{11}O_5Br$ requires Br, 22.8 per cent). It gave a violet colour with alcoholic ferric chloride and dissolved in alkali slowly without colour.

Fries Migration.— (*i*). An intimate mixture of (I : X=Br; 3.5 g., 1 *M*) and $AlCl_3$ (4.5 g., 3.3 *M*) was heated at 140°-150° for 1½ hours, cooled and decomposed with ice and HCl (5 c. c.). The solid was extracted with alkali (5%) when most of it dissolved. The solid obtained by acidifying the alkaline filtrate was collected and treated with sodium bicarbonate solution (5%), when a part of it dissolved with effervescence. The bicarbonate filtrate on acidification furnished a solid which was crystallised from dilute acetic acid as yellow fibrous needles, m. p. 206° (decomp.), yield 0.8 g. (Found : Br, 23.7. $C_{14}H_9O_5Br$ requires Br, 23.7 per cent).

The bicarbonate-insoluble portion after washing with water was crystallised from dilute alcohol as clusters of silky yellow needles, m. p. 133°, yield 1 g. (Found : Br, 22.5. $C_{15}H_{11}O_5Br$ requires Br, 22.8 per cent). Both the keto-ester and the acid dissolved in alkali with deep yellow colour and imparted a red colour with alcoholic ferric chloride solution.

(*ii*). The above isomerisation was carried out using dry nitrobenzene (40 c. c.) ($CaCl_2$ guard-tube) at 100° for 1 hour. It was decomposed as usual and nitrobenzene was steam-distilled. The residual liquid was filtered hot ; the brownish residue on the filter paper was extracted with dilute alkali (5%). The alkaline filtrate on acidification furnished a solid which on treatment with bicarbonate solution yielded the keto-acid, and the keto-ester was identified by their mixed m. p. with the migration products.

Friedel-Crafts Benzoylation of Methyl 2 : 4-Dihydroxy-5-bromobenzoate and the corresponding Acid.—The ester (3.0 g.) and benzoyl chloride (2.5 c.c.) were added with cooling to the solution of $AlCl_3$ in dry nitrobenzene (40 c. c.). The mixture was left overnight at room temperature and then heated at 115°-120° for 4 to 5 hours. On working it up as before, the keto-ester (II : R=Me ; X= Br) was obtained and identified by direct comparison with the same obtained before. A minute quantity of the keto-acid was also obtained.

The Friedel-Crafts benzoylation of 2 : 4-dihydroxy-5-bromobenzoic acid with benzoyl chloride under identical conditions as above yielded the keto-acid (II : R= H ;

X = Br) identified by mixed m. p. with a sample prepared by the hydrolysis of the keto-ester (II : R = Me ; X = Br).

Hydrolysis of the Keto-ester (II : R = Me ; X = Br).—The keto-ester (1 g.) was hydrolysed with 10% NaOH (20 c. c.) at room temperature for 24 hours and the same keto-acid, m. p. 206° (decomp.), was obtained.

The *diacetyl derivative of the keto-ester* (II : R = Me ; X = Br), prepared by H_2SO_4 drop method, crystallised from alcohol in colorless granules, m. p. 111°. (Found : Br, 18.1. $C_{19}H_{15}O_7Br$ requires Br, 18.3 per cent).

The *methyl ester of the keto-acid* (II : R = H ; X = Br), prepared by esterification with methyl alcohol in presence of a few drops of H_2SO_4 (conc.), crystallised from dilute alcohol in yellow needles, m. p. 133° ; mixed m. p. with the above keto-ester remained undepressed.

The *semicarbazone* of the *keto-ester* (II : R = Me ; X = Br), prepared as usual, crystallised from alcohol in needles, m. p. 205° (decomp.). (Found : N, 10.18. $C_{16}H_{14}O_5N_3Br$ requires N, 10.3 per cent).

Decarboxylation of the Keto-acid (II : R = H ; X = Br).—The acid (1 g.) in water (80 c. c.), acetic acid (3 c. c.) and HCl (conc., 2 c. c.) was refluxed on a sand-bath for 24 hours. The solution deposited yellow needles on cooling. It was washed with 5% bicarbonate solution and then with water and crystallised from hot water in lemon-yellow needles, m. p. 122-23° (0.3 g.), mixed m. p. with the hydrolysis product of 8-benzoyl-7-hydroxy-6-bromo-4-methylcoumarin (IV : X = Br) (Setalvad and Shah, *loc. cit.*) remaining undepressed.

2-Benzoyl-4-bromoresorcinol (III, X = Br) (0.5 g.) on the Pechmann condensation with ethyl acetoacetate (1 g.) in presence of $HgSO_4$ (80%, 30 c.c.) yielded 8-benzoyl-7-hydroxy-6-bromo-4-methylcoumarin (IV, X = Br), m. p. 235°, mixed m. p. with an authentic sample (*loc. cit.*) being undepressed.

Fries Migration of Methyl 2-Hydroxy-4-benzoyloxy-5-chlorobenzoate

Experimental details are omitted in this section for the sake of brevity, as they are generally indentical with those for the bromo compound, described above.

Methyl 2-hydroxy-4-benzoyloxy-5-chlorobenzoate (I X = Cl), prepared as before, crystallised form acetic acid in colorless needles, m. p. 157°. (Found : Cl, 11.7. $C_{15}H_{11}O_5Cl$ requires Cl, 11.6 per cent). It produced a violet colour with alcoholic ferric chloride and dissolved slowly in alkali without any colour.

Fries Migration of (I : X = Cl).—(*i*). The benzoyl ester (I : X = Cl ; 3 g., 1 *M*) and $AlCl_3$ (4.5 g., 3.3 *M*) were heated at 135°-140° as before ; on working it up similarly methyl 2 : 4-dihydroxy-3-benzoyl-5-chlorobenzoate (II : R = Me ; X = Cl) crystallised from alcohol in yellow silky needles, m. p. 161° (0.8 g.). (Found : Cl, 11.3. $C_{15}H_{11}O_5Cl$ requires Cl, 11.6 per cent).

The bicarbonate solution on acidifying furnished the keto-acid (II : R = H ; X = Cl) which crystallised from hot water in needles, m p. 181° (decomp.), identical with the same obtained by the hydrolysis of (II : R = Me ; X = Cl) by 10% alkali. (Found :

Cl, 12.4. $C_{14}H_9O_5Cl$ requires Cl, 12.2 per cent). Both the keto-ester and the acid dissolved in alkali with a yellow colour and gave a reddish brown colour with alcoholic ferric chloride.

(*ii*). The above migration was also carried out in nitrobenzene as the solvent, the same keto-ester and acid being obtained.

The Friedel-Crafts benzoylation of methyl 2:4-dihydroxy-5-chlorobenzoate and the free acid under similar conditions, described for the bromo compound, furnished the keto-ester and acid, identical with the migration product, in good yield.

The *diacetyl derivative* of the keto-ester (II: R = Me; X = Cl) crystallised from alcohol in colorless needles, m. p. 146°. (Found: Cl, 9.3. $C_{19}H_{15}O_7Cl$ requires Cl, 9.1 per cent).

The *methyl ester of the acid* (II: R = H; X = Cl), obtained by the usual esterification, melted at 161°, mixed m. p. with the migration product being the same.

The keto-acid (II: R = H; X = Cl) on decarboxylation as before furnished (III, X = Cl) which crystallised from hot water in lemon-yellow needles, m. p. 119-20°, yield 30%, identical with the hydrolysis product of 8-benzoyl-7-hydroxy-6-chloro-4-methylcoumarin (IV, X = Cl) (Setalvad and Shah, *loc. cit.*).

2-Benzoyl-4-chlororesorcinol (III, X = Cl) underwent the Pechmann reaction affording 8-benzoyl-7-hydroxy-6-chloro-4-methylcoumarin (IV, X = Cl); it crystallised from acetic acid in pale yellow plates, m. p. 255°, mixed m. p. with the same obtained before (*loc. cit.*) remaining undepressed.

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DEPENDENCE OF R_F VALUES OF AMINO-ACIDS ON THE SHAPE AND SIZE OF THE FILTER PAPER

By H.C. Chakrabortty and D. P. Burma

The dependence of R_F values of two amino-acids, serine and valine, on the shape and size of the filter paper has been investigated with a view to studying the transition from linear to circular chromatography. The R_F values are affected very little by the width of the strip or the sector angle. It has been shown both experimentally and theoretically that the R_F values on strips are equal to the squares of those on sectors or in circular chromatography.

The greater value of R_F in circular chromatography (R_FC) than in the strip chromatography (R_FL) has been observed by a number of workers (Rao and Giri, *J. Ind. Inst. Sci.*, 1953, **35**, 77; Chakrabortty and Burma, *Curr. Sci.*, 1953, **22**, 238). In fact a relation between the two in the form, $(R_FC)^2 = R_FL$, has been deduced and experimentally verified (Lestrange and Müller, *Anal. Chem.*, 1954, **26**, 953; Ganguli, *Anal. Chim. Acta*, 1955, **12**, 335). The transition from linear to circular chromatography may be studied by introducing sector-shaped filter paper of varying angles in place of strips. It has been observed that as soon as an angular cut is made, the R_F becomes large and then increases only slightly as the sector is widened, and approaches the value corresponding to circular chromatography (Chakrabortty and Burma, *loc. cit.*). Müller and Clegg (*Anal. Chem.*, 1951, **23**, 403) studied the influence of size and shape of filter paper strips on the rates of liquid flow and concluded that a narrow strip ensured a greater speed. Assuming a constant volume of the solvent flowing in unit time, this is quite expected.

It may be observed that in sector chromatography, the width of the paper varies continuously, whereas in strips the same remains unaltered. It is therefore of interest to study if width variation of strips has any effect on R_F. It has been shown below that R_F values on sector-shaped paper are almost equal to the squares of those on the strip. Simultaneously, the effect of varying the sector-angles on R_F has also been studied.

Experimental

Filter paper strips of varying width were employed for determining R_F values of serine and valine by both the descending and the ascending techniques using phenol-water as the developing solvent. The strips and the sectors were initially marked at 4, 8 and 12 cm. distances, the object being to stop the development as soon as the solvent front in all the strips and sectors had traversed nearly the same distance. The corresponding times were also noted. The strip width varied from 0.5 cm. to 10 cm. and the sectors from 10° to 40°. The rest of the experimental arrangements was the same as those employed earlier in this laboratory (Sen and Burma, *Trans. Bose Res. Inst.*, 1952-53, **19**, 19; Burma, D. Phil. Thesis, Calcutta University, 1951). All the strips and sectors were accommodated in a chamber for two-dimensional chroma-

tography. Approximately 10 μg. portion of the amino-acids were applied with a micro-dropper at 1 cm. depth from one end of the strip in the ascending method and 5 cm. from the end in the descending method. The amino-acids were applied at 1 cm. from the apex of the sector in the ascending technique.

TABLE I

Effect of the width of the strip on R_F values and the rate of movement of the developing solvent.

Solvent: Phenol-water. Temp. = 30 ± 1°; *d*, distance in cm. traversed by the solvent front. (Ascending technique).

Strip width	0.5 cm.		2.5 cm.		5 cm		10.0 cm.	
Time.	*d*	R_F.	*d*	R_F.	*d*	R_F.	*d*	R_F.
				Serine				
30 min.	5.5	0.43	6.1	0.37	6.1	0.37	6.1	0.38
105	8.0	0.45	9.05	0.41	9.0	0.42	9.25	0.42
195	12.7	0.44	13.9	0.43	12.4	0.41	12.5	0.40
				Valine				
30	5.7	0.83	5.95	0.80	5.9	0.80	6.0	0.80
105	8.95	0.83	9.3	0.82	9.3	0.82	9.35	0.83
195	12.6	0.84	14.85	0.84	13.0	0.84	12.8	0.85

TABLE II

Effect of the angle of the sector on R_F values and the rate of movement of the developing solvent.

Conditions same as in Table I.

Angle of the sector	10°		20°		30°		40°	
Time.	*d*	R_F.	*d*	R_F.	*d*	R_F.	*d*	R_F.
				Serine				
60 min.	5.3	0.53	5.2	0.54	5.35	0.52	4.95	0.53
155	8.6	0.55	7.75	0.57	7.95	0.55	7.75	0.56
345	12.2	0.57	12.1	0.57	11.8	0.57	12.35	0.55
				Valine				
60	5.35	0.88	5.45	0.87	4.8	0.87	4.95	0.85
155	8.2	0.86	7.95	0.84	8.75	0.85	8.7	0.85
345	12.7	0.85	11.8	0.85	11.5	0.86	12.5	0.85

TABLE III

Effect of the width of the strip on R_F values and the rate of movement of the developing solvent.

Solvent: Phenol-water. Temp. = 30 ± 1°. *d*, distance in cm. traversed by the solvent front. (descending technique).

Time	Strip width 0.5 cm.		1.0 cm.		1.5 cm.		2.0 cm.		2.5 cm.		3.0 cm	
	d	R_F.	*d*	R_F.	*d*	R_F.	*d*	R_F.	*d*	R_F.	*d*	R_F.
	Serine											
40 min.	5.05	0.36	4.45	0.35	4.8	0.36	4.95	0.38	4.85	0.35	4.0	0.35
80	8.55	0.37	8.2	0.37	8.4	0.38	8.5	0.37	8.6	0.37	8.2	0.36
155	12.15	0.37	12.3	0.35	12.45	0.38	11.9	0.85	11.9	0.36	12.4	0.36
	Valine.											
40	4.75	0.78	4.75	0.75	5.15	0.77	4.7	0.78	5.3	0.80	4.2	0.78
80	8.25	0.76	8.65	0.76	8.55	0.77	8.65	0.78	8.4	0.77	8.1	0.75
155	12.2	0.75	2.55	0.75	12.05	0.76	12.45	0.77	11.8	0.75	12.5	0.77

DISCUSSION

The following points emerge from the results recorded in Tables I to III.

In the ascending technique the rate of movement of the solvent is initially fairly high but slows down towards the end; this takes place irrespective of the width of the papers, but the R_F value is affected little except on the narrowest, on which the R_F shows a slight increase. It must, however, be pointed out that other small variations in the rate of movement, as they appear from the data, may be ascribed to the small differences in the capillary system of the paper itself.

In the descending technique the initial rate is not very much different. This is possible due to the fact that the solvent front is here measured after the initial 5 cm. distance has been traversed. The R_F values obtained by this technique are slightly lower than those obtained by the ascending technique. Similar results were also previously recorded (Burma, this *Journal*, 1952, **29**, 567). This variation arises from the lack of the necessary conditions of saturation in the ascending technique. As might be expected with a more volatile solvent mixture, *e.g.*, butanol-aceticacid-water, much wider variations were observed.

For the same strip, the R_F values, calculated for different distances (4, 8 and 12 cm.) of the solvent front, do not vary appreciably from one another.

The R_F values observed with the sector-shaped filter papers using the ascending technique were much higher than similar values on strips, particularly with one of the amino-acids, viz., serine. In the case of valine, the values are already too large and, hence, greater variations are not expected. The effect of varying the angle from 10° to 40° on the R_F values is not quite appreciable. The R_F values by circular chromatography are respectively 0.54 and 0.84 for serine and valine as against the corresponding average values 0.56 and 0.85 on sectors.

Let us consider a strip of paper and a sector of any angle on each of which a chromatogram has been obtained. The volumes traversed by the solvent (V_2) and solute (V_1) fronts on the strip are related as follows:

$$\frac{V_1}{V_2} = \frac{l_1 \times b \times d \times f_1}{l_2 \times b \times d \times f_2}$$

where the lengths, breadths and thicknesses are denoted by l, b and d, and f_1 and f_2 are the accommodation coefficients which are likely to be different for the solute and the solvents. If the same volumes are allowed to traverse the radial distances, r_1, and r_2, in the sector chromatogram, then

$$\frac{V_1}{V_2} = \frac{k \times r_1^2 \times d \times f_1}{k \times r_2^2 \times d \times f_2}$$

since the areas of the sectors will be proportional to the squares of their radii.

Hence, $$\frac{l_1}{l_2} = R_F \text{ (linear)} = \frac{r_1^2}{r_2^2} = \left(\frac{r_1}{r_2}\right)^2 = \left(R_F \text{ sector}\right)^2$$

The same relation will hold good for the circular chromatogram as, in fact, has been shown by Ganguli (*loc. cit.*).

In view of the fact that filter paper in the form of even a small angle influences the R_F values so markedly, the experiments on strips were at first made by varying the width at narrower intervals, viz. 0.5 cm. Results recorded in Table III show that the effect is almost negligible and varies little from those observed on much wider strips (cf. Table I). In order to ensure reproducible R_F values on strips, it is extremely necessary, as the results on sector chromatograms have shown, to cut the strips perfectly rectangular, for even a small angle might vitiate the results.

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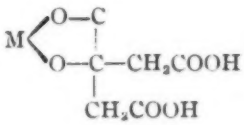
CITRATE COMPLEX OF TRIVALENT ANTIMONY

By R. Das and S. Pani

Citrate complex of trivalent antimony has been investigated by the solubility method. The complex contains one citrate ligand per atom of antimony. The complex I formed by the interaction of antimonyl and dihydrogen citrate ions behaves as a dibasic acid and dissociates in two steps (a and b) to complex II and III respectively.

The complex III reacts at higher p_H to furnish hydrated antimony oxide and citrate ion. The equilibrium constant of all the reactions has been calculated.

In oxalate and lactate complexes of trivalent antimony (Nanda and Pani, this *Journal*, 1954, **31**, 588; Mohanty and Pani, *ibid.*, 1954, **31**, 503) the co-ordination number of antimony is four. Citric acid is a monohydroxy tribasic acid. The hydroxyl group is at α-position to one of the carboxyl groups and at β-position to the other two. If the antimony combines with the central carboxyl group and the hydroxyl group, the citrate complex might contain two citrate ligands per atom of antimony. A complex containing two citrate ligands has been reported by Volman and Gottelmann (*Compt. rend.*, 1942, **215**, 417). If the ligand would react like lactate, it would occupy two co-ordination positions as shown below.



If the above complex is examined, one can see that out of the two unreacted carboxyl groups in the citrate ligand, one can be very near to the 'M' atom, and a six-membered ring might be formed besides the five-membered ring shown above. If this takes place, citrate ligand would behave as tridentate. If the co-ordination number of antimony in these complexes cannot be more than four (as seen in lactate and oxalate complexes) and if citrate ligand would behave as a tridentate ligand, the citrate complex of antimony is expected to contain one citrate ligand per atom of antimony. It is therefore worthwhile to investigate the citrate complex of antimony.

The solubility of antimony oxide in partially neutralised citric acid solution of known concentration was determined and the p_H of the solution was measured. The experimental procedure is similar to that followed in the case of lactate complex of antimony (Mohanty and Pani, *loc.cit.*). The results are shown in Table I.

TABLE I

Ratio of acid to salt.	Total citrate [Cit]	Total antimony [SbC].	Unreacted citrate ([Cit]−[SbC]).	Citrate ion [Cit^{3-}].	p_H	K_I.	K_{II}.	K_{III}.
Pure	1.00	0.09090	0.9091	5.914×10^{-10}	1.26	1.585×10^{5}	2.189×10^{8}	2.633×10^{12}
acid	0.80	0.07110	0.7287	8.215×10^{-10}	1.34	1.552	1.741	2.46×10^{12}
	0.50	0.04910	0.4509	1.328×10^{-9}	1.48	1.743	1.417	1.45×10^{12}
	0.20	0.01890	0.1818	1.067×10^{-8}	1.92	1.744	0.5144	1.911×10^{11}
	0.10	0.00925	0.09075	2.346×10^{-8}	2.14	1.619	0.2878	7.066×10^{10}
4 :1	1.00	0.1372	0.8628	1.069×10^{-5}	2.74	3.648×10^{5}	1.629×10^{7}	9.162×10^{9}
	0.80	0.1047	0.6953	1.103×10^{-5}	2.78	3.558	1.450	7.433
	0.50	0.07085	0.4291	7.683×10^{-6}	2.80	3.966	1.543	7.556
	0.20	0.02600	0.1740	6.400×10^{-6}	2.92	4.002	1.181	4.388
	0.10	0.01162	0.08838	1.158×10^{-5}	3.06	2.600	0.5559	1.496
2 :1	1.00	0.1459	0.8541	6.748×10^{-4}	3.48	1.02×10^{6}	8.285×10^{8}	8.478×10^{8}
	0.80	0.1129	0.6871	5.493 ,,	3.48	0.9692	7.877	8.061
	0.50	0.0711	0.4281	4.554 ,,	3.54	1.114	7.889	7.031
	0.20	0.0262	0.1738	2.998 ,,	3.64	1.303	6.997	4.953
	0.10	0.01185	0.08815	2.017 ,,	3.70	1.267	6.203	3.824
4 :3	1.00	0.1485	0.8515	9.309×10^{-3}	4.06	4.133×10^{6}	8.837×10^{6}	2.379×10^{9}
	0.80	0.1185	0.6815	8.071 ,,	4.08	4.368	8.919	2.293
	0.50	0.0717	0.4213	5.493 ,,	4.10	4.459	8.694	2.134
	0.20	0.02643	0.1736	3.035 ,,	4.18	5.169	8.383	1.712
	0.10	0.01209	0.08791	2.395 ,,	4.30	6.861	8.441	1.307
1 :1	1.00	0.1495	0.8505	$4.01\cdot10^{-2}$	4.46	1.531×10^{7}	1.303×10^{7}	1.396×10^{9}
	0.80	0.1207	0.6793	3.202 ,,	4.46	1.548	1.317	1.412
	0.50	0.0727	0.4273	2.599 ,,	4.54	1.996	1.414	1.260
	0.20	0.02702	0.1729	1.504 ,,	4.66	2.936	1.577	1.066
	0.10	0.01204	0.08786	0.9561 ,,	4.74	3.608	1.612	0.906
3 :4	1.00	0.1513	0.8487	0.1082	4.80	6.010×10^{7}	2.338×10^{7}	1.145×10^{9}
	0.80	0.1214	0.6786	0.1058	4.88	8.574	2.774	1.131
	0.50	0.0728	0.4272	0.06661	4.88	8.168	2.643	1.076
	0.20	0.0271	0.1729	0.03559	5.00	13.03	3.200	0.988
	0.10	0.0122	0.0878	0.01807	5.00	14.55	2.836	0.8766
1 :2	1.00	0.1439	0.8561	0.3951	5.46	1.496×10^{9}	1.274×10^{8}	1.364×10^{9}
	0.80	0.1118	0.6882	0.3176	5.46	1.445	1.230	1.318
	0.50	0.0695	0.4305	0.2095	5.50	1.795	1.393	1.361
	0.20	0.0243	0.1757	0.08999	5.54	1.930	1.366	1.217
	0.10	0.0102	0.0898	0.04595	5.54	1.584	1.121	0.9995

It is assumed that n citrate ligands, Ct (dihydrogen citrate ion H_2Cit^- or monohydrogen citrate ion $HCit^{2-}$ or citrate ion Cit^{3-}), react with an antimonyl ion and the complex SbC, m hydrogen ions and a molecule of water are produced (if n is equal to one, a molecule of water might not be produced). The reaction is represented by equation (1). The complex SbC may be neutral or an ion.

$$SbO^+ + nCt \rightleftharpoons SbC + mH^+ + H_2O \quad \ldots \quad \ldots \quad (1)$$

If the complex is an ion, the number of charge and the value of m would depend on the particular citrate ligand taking part in the reaction, the value of n and the number of co-ordination positions occupied by the ligand.

The equilibrium constant is given by equation (2) where $[SbO^+]$, [Ct], [SbC] and $[H^+]$ represent the molar concentrations of antimonyl ion, the citrate ligand which reacts with antimonyl ion, the complex and hydrogen ion respectively.

$$\frac{[SbC] \times [H^+]^m}{[SbO^+] \times [Ct]^n} = K \quad \ldots \quad \ldots \quad (2)$$

The concentration of antimonyl ion is equal to $7.7 \times 10^{-4} \times [H^+]$ (Gayer and Garrett, *J. Amer. Chem. Soc.*, 1952, **74**, 2353). Substituting this in equation (2) and taking concentration of hydrogen ion to be constant in each set of experiments, we get

$$\frac{[SbC]}{[Ct]^n} = K_1 \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

The total citrate, [Cit], is equal to the sum of the concentrations of the citric acid, $[H_3Cit]$, dihydrogen citrate ion $[H_2Cit^-]$, monohydrogen citrate ion $[HCit^{2-}]$, citrate ion $[Cit^{3-}]$ and citrate present in the complex, n [SbC].

$$[Cit] - n[SbC] = [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}] \quad \ldots \quad (4)$$

It can be shown that

$$[Cit^{3-}] = \frac{k_3}{[H^+]}[HCit^{2-}] = \frac{k_2.k_3}{[H^+]^2}[H_2Cit^-] = \frac{k_1.k_2.k_3}{[H^+]^3}[H_3Cit] \quad \ldots \quad (5)$$

where k_1, k_2 and k_3 are respectively first, second and third dissociation constant of citric acid. Hence

$$[Cit] - n[SbC] = \text{unreacted citrate} = [Cit^{3-}]\left\{1 + \frac{k_3}{[H^+]} + \frac{k_2.k_3}{[H^+]^2} + \frac{k_1.k_2.k_3}{[H^+]^3}\right\} \quad (6)$$

If the concentration of hydrogen ion is constant, the concentration of citrate ion is proportional to the concentration of unreacted citrate, citric acid, dihydrogen citrate ion, monohydrogen citrate ion and to citrate ion. Hence, whichever species of citrate ion reacts, for each set of experiments (citric acid has been neutralised to the same extent and p_H is very nearly constant)

$$\frac{[SbC]}{([Cit] - n[SbC])^n} = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

If log [SbC] is plotted against log $([Cit] - n[SbC])$, a straight line would be obtained and the slope would give the value of n.

The solubility of antimony oxide in water being very small compared to that in citrate solution, the whole of antimony in the solution is taken to be present as complex. Two sets of values of concentrations of unreacted citrate were calculated by assuming n to be equal to 1 and 2 respectively, and the logarithms of the concentration of unreacted citrate were plotted against the corresponding log [SbC]. In

each set straight lines were obtained and the value of n was found to be very nearly one.

The citrate ligand is most probably tridentate. The co-ordination number of antimony is assumed to be four. The reactions can be represented by equations (I), (II) and (III) according as dihydrogen citrate ion, monohydrogen citrate ion or citrate ion with antimonyl ion reacts with antimonyl ion. The corresponding equilibrium constants are given by equations (I-1), (II-1) and (III-1) respectively.

$$SbO^{+} + H_2Cit^{-} \rightleftharpoons \left[H_2O-Sb(-O-C(=O)-O-)-C(-CH_2COOH)(-CH_2-)-C(=O)-O \right] \quad \ldots \quad (I)$$

$$\frac{[SbC_1]}{7.7\times10^{-4}\times[H^{+}][H_2Cit^{-}]} = K_I \quad \ldots \quad (I\text{-}1)$$

$$SbO^{+} + HCit^{2-} \rightleftharpoons \left[H_2O-Sb(-O-C(=O)-O-)-C(-CH_2COO)(-CH_2-)-C(=O)-O \right]^{-} \quad \ldots \quad (II)$$

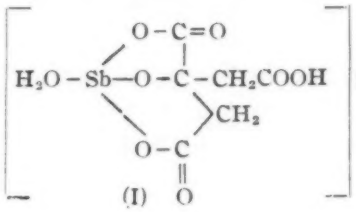
$$\frac{[SbC_2]}{7.7\times10^{-4}[H^{+}]\times[HCit^{2-}]} = K_{II} \quad \ldots \quad (II\text{-}1)$$

$$SbO^{+} + Cit^{3-} \rightleftharpoons \left[HO-Sb(-O-C(=O)-O-)-C(-CH_2COO)(-CH_2-)-C(=O)-O \right]^{2-} \quad \ldots \quad (III)$$

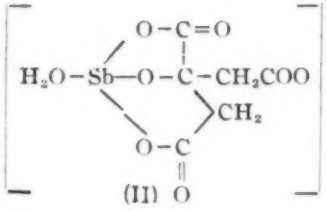
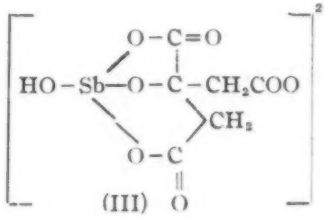
$$\frac{[SbC_3]}{7.7\times10^{-4}\times[H^{+}]\times[Cit^{3-}]} = K_{III} \quad \ldots \quad (III\text{-}1)$$

It is assumed that either reaction (I) or (II) or (III) takes place, hence $[SbC_1]$, $[SbC_2]$, $[SbC_3]$, the concentrations of the complexes, would be equal to the total antimony present in one litre of the solution. $[Cit^{3-}]$ is calculated by equation (6) using the values k_1, k_2 and k_3 to be 8.32×10^{-4}, 4.07×10^{-5} and 3.24×10^{-6} respectively (Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1949, **32**, 1682). The calculated values of K_I, K_{II} and K_{III} are shown in Table I.

None of these equilibrium constants are actually constant throughout the investigation. K_I can be taken as constant at the beginning. It slowly increases first, then very rapidly with increasing p_H. K_{II} is not constant at the lower p_H range. It first decreases, becomes very nearly constant and then increases with increasing p_H. The variation of K_{III} is just opposite to K_I. It is very nearly constant in the higher p_H range. It is interesting to note that only particular constant is very nearly constant at a certain p_H range, whereas the other two are not. All the three species of complexes :

Complex I, 

(I)

Complex II,  ; Complex III, 

(II) (III)

probably exist. The equilibrium constants K_I , K_{II} and K_{III} being constant at different but definite p_H ranges, a particular species of the complex exists in solution in large concentrations only at a definite p_H range, whereas the concentrations of the other two are small. The process is, however, expected to be continuous. The complex I exists in pure citric acid medium. As the p_H is gradually increased, it dissociates into hydrogen ion and complex II. At still higher p_H, the complex II dissociates into hydrogen ion and the complex III. The complex I therefore is a dibasic acid. The formation of the complex I is represented by reaction (I). The dissociation of this complex in two steps is given by reactions (a) and (b).

$$[I] \rightleftharpoons H^+ + [II]^- \quad \ldots \quad \ldots \quad (a)$$

$$[II]^- \rightleftharpoons H^+ + [III]^{2-} \quad \ldots \quad \ldots \quad (b)$$

$$\frac{[Sb_{II}][H^+]}{[Sb_I]} = K_a \quad \ldots \quad \ldots \quad (a\text{-}1)$$

$$\frac{[Sb_{III}] \times [H^+]}{[Sb_{II}]} = K_b \quad \ldots \quad \ldots \quad (b\text{-}1)$$

The equilibrium constant of reactions (a) and (b) are given by equations (a-1) and (b-1) respectively where $[Sb_I]$, $[Sb_{II}]$ and $[Sb_{III}]$ represent the molar concentrations of the first, second and third complex respectively.

The antimony content of the solution containing a fixed amount of citrate increases with increasing p_H but decreases after p_H 5. (It can be further added here that solubility of antimony oxide in sodium citrate solution is very small). This decrease in solubility cannot be explained by the above reaction. Another reaction by which antimony is removed from the solution probably takes place as follows.

$$[III]^{2-} + OH^- + H_2O \rightleftharpoons Sb(OH)_3 + HO-\underset{\displaystyle CH_2COO}{\overset{\displaystyle CH_2COO^{3-}}{\overset{|}{\underset{|}{C}}}}-COO \qquad \ldots \text{(c)}$$

The equilibrium constant is given by the reaction :

$$\frac{[Cit^{3-}]}{[Sb_{III}] \times [OH^-[} = K_c. \qquad \ldots \text{(c-1)}$$

TABLE II

p_H.	$[Cit^{3-}]$.	$[Sb_I]$.	$[Sb_{II}]$.	$[Sb_{III}]$.	$K_1 \times 10^{-5}$.	$K_2 \times 10^3$.	$K_3 \times 10^5$.	$K_c \times 10^9$.
1.26	5.914×10^{-10}	0.09090			1.586			
1.34	8.215×10^{-10}	0.07110			1 552			
1 48	1.328×10^{-9}	0.04910			1.743			
1.92	1.067×10^{-8}	0.01850			1.744			
2.14	2.346×10^{-8}	0.009250			1.616			
2.74	1.069×10^{-5}	0.06222	0.06498		Mean	1.900		
2.78	1.103×10^{-5}	0.04867	0.05603		value of	1.911		
2.80	7.683×10^{-6}	0.02955	0.04130		K_1	2.217		
2 92	6.400×10^{-6}	0.01074	0.01526		1.653×10^5	1.708		
3 06	1.158×10^{-5}	0.007389	0 00427			...		
3.48	6.748×10^{-4}	0.02367	0.1222			1.716		
3.48	5.493×10^{-4}	0.01927	0.09263			1.592		
3.54	4.554×10^{-4}	0.01055	0 06055			1.656		
3.64	2.998×10^{-4}	0.003482	0.02272			1.495		
3 70	2.017×10^{-4}	0.001547	0.01030			1 327		
4.06	9.309×10^{-3}	5.939×10^{-3}	0.1426			2 091		
4 08	8.071×10^{-3}	4.487×10^{-3}	0.1140			2.113		
4 10	5.493×10^{-3}	2.650×10^{-3}	0.06904			2.062		
4 18	3.035×10^{-3}	0.8455×10^{-3}	0.02559			1.979		
4 30	2.395×10^{-3}	0.2913×10^{-3}	0.01180			2.031		
4.46	4.010×10^{-2}	$1 614 \times 10^{-3}$	0.08586	0.06204		Mean	2.564	2.241
4 46	3.202×10^{-2}	1.289×10^{-3}	0.06857	0.05083		value of	2.571	2.186
4 54	$2 599 \times 10^{-2}$	$0 6023 \times 10^{-3}$	0 03850	0 03360		K_2	2.517	2.230
4.66	1.504×10^{-2}	0.1522×10^{-3}	0.01282	0.01405		1.884×10^{-3}	2 397	2.342
4.74	$0 9561 \times 10^{-2}$	0.0639×10^{-3}	0 006183	0.005897			1.818	3.089
4.80	0 1082	4.161×10^{-4}	0.04841	0.1025			3.356	1.673
4 88	0.1058	2.341×10^{-4}	0 03274	0.08846			3.362	1.576
4 88	0.06661	1.474×10^{-4}	0 02062	0.05203			3 326	1.689
5 00	0.03559	0.3430×10^{-4}	0.006324	0.02075			3.282	1 715
5 00	0 01807	0.1746×10^{-4}	0.003219	0 00896			2.784	2 019
5.46	0.3951	1.592×10^{-5}	8.461×10^{-3}	0 1354			5.549	1.012
5.46	0.3176	$1 279 \times 10^{-5}$	6.801×10^{-3}	0.1050			5.353	1.049
5.50	0.2097	6.403×10^{-6}	3.734×10^{-3}	0 06577			5 572	1.008
5.54	0 08999	2.085×10^{-6}	1.333×10^{-3}	0 02297			4.969	1.130
5.54	0.04595	1.065×10^{-6}	0.6808×10^{-3}	0 009519			4.033	1.392
							Mean value of K_3	Mean value of K_c
							3.563×10^{-5}	1.737×10^{-9}

The total antimony in the solution [SbC] is equal to the sum of the concentrations of Sb_I, Sb_{II} and Sb_{III}. The concentrations of Sb_{II} and Sb_{III} are assumed to be negligible in the first series of experiments. The mean value of K_1 (1.653×10^5) in the first series of experiments is taken as the actual value of K_1. $[Sb_I]$ is calculated for the other series of experiments. The difference of the concentrations of total antimony [SbC] and $[Sb_I]$ is equal to the sum of the concentrations of Sb_{II} and Sb_{III}. It is again assumed that the concentration of Sb_{III} is very small in the first few series. Hence, ([SbC]-$[Sb_I]$) is taken as equal to $[Sb_{II}]$, and K_a is calculated. It is found that K_a is almost constant in 2nd, 3rd and 4th series of experiments and increases appreciably after this. The mean value of K_a (1.884×10^{-3}) in the 2nd, 3rd and 4th series is taken as the value of K_a, and $[Sb_{II}]$ is calculated for the other three series. $[Sb_{III}]$ is obtained by subtracting the concentrations of Sb_I and Sb_{II} from [SbC]. K_b is calculated and shown in Table II.

It is interesting to note that K_b and K_c are fairly constant and the mean values are 3.563×10^{-5} and 1.737×10^{-9} respectively.

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CHLORAMINE-B AS A VOLUMETRIC REAGENT

By Apar Singh

Chloramine-B has been used for the potentiometric estimation of hydroquinone, hydrazine sulphate, tartar emetic, quinhydrone, phenylhydrazine, $K_4Fe(CN)_6$, As_2O_3, $FeSO_4$ and KI in acid medium.

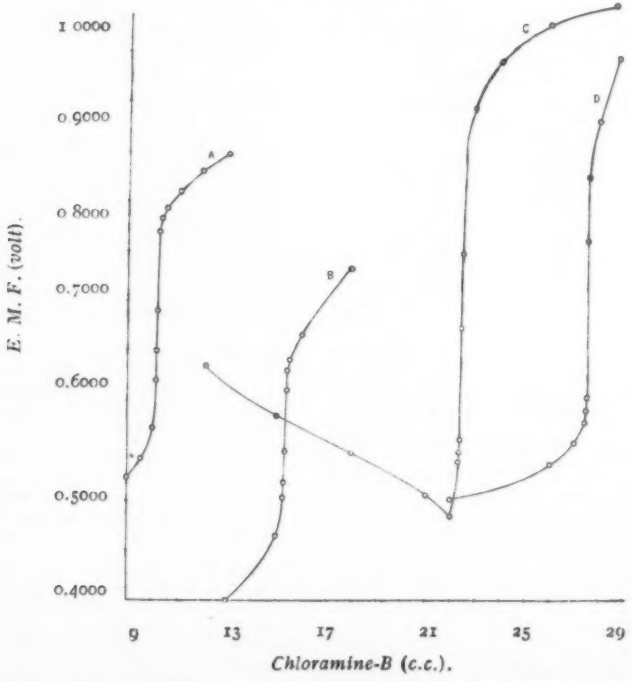
Chloramine-B, the sodium derivative of N-chlorobenzenesulphonamide, in aqueous solution is hydrolysed to hypochlorite which is responsible for its oxidising action in solution.

$$C_6H_5SO_2N(Na)Cl + H_2O \longrightarrow C_6H_5SO_2NH_2 + NaClO.$$

B.N. Afana'seve (*Sverdlovsk Agr. Inst. Zavodskaya Lab.*, 1950, **16**, 1011) has reported that Chloramine-B is a good substitute for Chloramine-T in analytical chemistry.

In the present investigation Chloramine-B has been used for the potentiometric estimation of hydroquinone, hydrazine sulphate, tartar emetic, quinhydrone, phenylhydrazine, potassium ferrocyanide, arsenious oxide, ferrous sulphate and potassium iodide in an acid medium.

FIG. 1



Curves A-D represent respectively hydroquinone, hydrazine, tartar emetic and quinhydrone.

The reaction of chloramine-B with potassium iodide as a typical of the series is represented by the equation

$$C_6H_5SO_2N(Na)\,Cl + 2KI + 2H_2O \longrightarrow C_6H_5SO_2NH_2 + 2KOH + 2NaCl + I_2.$$

EXPERIMENTAL

The oxidation-reduction electrode, which consisted of a bright platinium foil immersed in a solution to be titrated, was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water-bath at 20°. E.M.F. of the cell was read on a potentiometer.

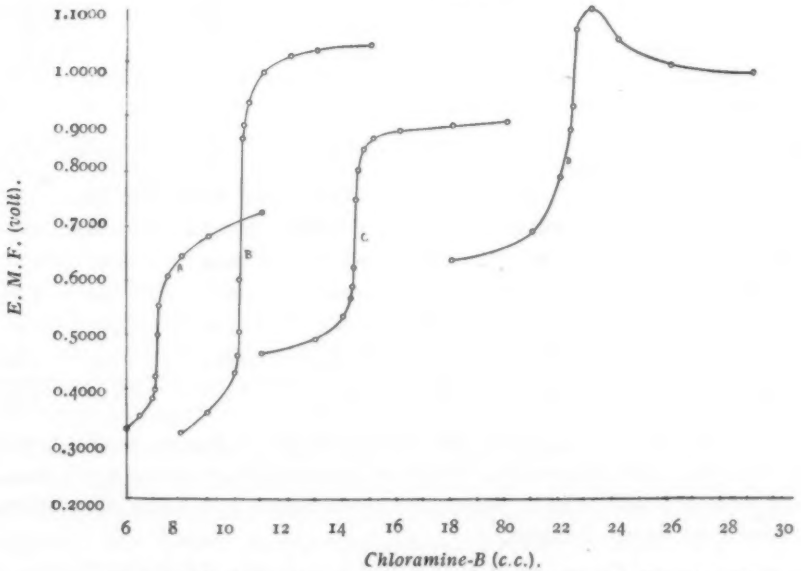
A known weight of the each substance was dissolved in water, acidified with a few c.c. of HCl, and titrated against a standard solution of Chloramine-B. In all these titrations the reaction mixture was kept stirred by a mechanical stirrer.

Potentiometric titrations were performed with different amounts of each substance. The titrations, one for each substance, are represented by the curves shown in Figs 1 and 2.

DISCUSSION

In these titrations it is evident that with the addition of the standard Chloramine-B solution, the E.M.F. rises steadily till the equivalence point. At the equivalence point there is a sharp jump in potential, followed by a steady rise in each case.

FIG. 2



Curves A-D represent respectively pot. ferrocyanide, As_2O_3,KI and $FeSO_4$.

From the amount of Chloramine-B used, corresponding to the equivalence point in each titration, the amount of each substance was calculated. In the following tables the calculated values are compared with the amounts of the substances taken.

TABLE I

Hydroquinone.				Hydrazine sulphate.	
C.B. used.	Taken.	Found.	C B. used	Taken.	Found.
0.0936 g.	0.0385 g.	0.0385 g.	0.0936 g.	0.0228 g.	0.0227 g.
0.1339	0.0550	0.0551	0.1338	0.0325	0.0325
0.2007	0.0825	0.0826	0.2007	0.0488	0.0488
0.2941	0.1211	0.1211	0.2940	0.0715	0.0714
0.3610	0.1487	0.1486	0.3609	0.0878	0.0877
0.4413	0.1818	0.1817	0.4416	0.1073	0.1073
	Tartar emetic.			Quinhydrone.	
0.0936	0.1169	0.1168	0.0936	0.0763	0.0763
0.1339	0.1670	0.1671	0.1339	0.1090	0.1091
0.2008	0.2505	0.2507	0.2007	0.1635	0.1636
0.2942	0.3647	0.3672	0.2942	0.2398	0.2397
0.3610	0.4509	0.4507	0.3610	0.2943	0.2941
0.4412	0.5511	0.5509	0.4412	0.3597	0.3595
	Phenylhydrazine hydrochloride.			Potassium ferrocyanide.	
0.0936	0.0506	0.0505	0.0935	0.2957	0.2953
0.1338	0.0723	0.0723	0.1339	0.4224	0.4228
0.2007	0.1083	0.1084	0.2008	0.6335	0.6339
0.2940	0.1590	0.1588	0.2941	0.9293	0.9287
0.3608	0.1951	0.1948	0.3609	1.1404	1.1400
0.4415	0.2383	0.2385	0.4412	1.3938	1.3932

TABLE II

Arsenious oxide.			Ferrous sulphate.			Potassium iodide.		
C.B. used.	Taken.	Found.	C.B. used.	Taken.	Found.	C.B. used	Taken.	Found.
0.0934 g.	0.0345 g.	0.0346 g.	0.0936 g.	0.1946 g.	0.1946 g	0.0936 g	0.1162 g.	0.1162 g.
0.1338	0.0495	0.0495	0.1339	0.2780	0.2781	0.1338	0.1660	0.1661
0.2007	0.0742	0.0742	0.2007	0.4170	0.4170	0.2008	0.2490	0.2491
0.2941	0.1088	0.1087	0.2941	0.6116	0.6112	0.2943	0.3652	0.3653
0.3610	0.1335	0.1335	0.3609	0.7506	0.7503	0.3613	0.4482	0.4484
0.4410	0.1632	0.1633	0.4412	0.9174	0.9170	0.4415	0.5472	0.5479

From the above results it is evident that hydroquinone, hydrazine sulphate, tartar emetic, quinhydrone, phenylhydrazine, potassium ferrocyanide, arsenious oxide, ferrous sulphate and potassium iodide can be determined potentiometrically using Chloramine-B as an oxidising agent in acid medium.

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ACTION OF SULPHUR DIOXIDE WATER ON CALCIUM PERMANGANATE

By Kundan Lal and Gurdev Singh

Normal sulphurous acid, when reacts with calcium permanganate (100 c.c., 1%), produces calcium sulphate, calcium dithionate, manganese sulphate and sulphuric acid. The reaction in the final stage, when continuous addition of sulphurous acid redissolves the precipitate formed during the reaction, may be represented by the equation,

$$5\ Ca(MnO_4)_2 + 26\ H_2SO_3 = 4\ CaSO_4 + 10\ MnSO_4 + CaS_2O_6 + 10\ H_2SO_4 + 16\ H_2O.$$

In the preceding communications (Lal and Singh, this *Journal* 1954, **31**, 410; 1955, **32**, 65), the action of potassium sulphite on potassium permanganate and of sulphurous acid on alkaline potassium permanganate have been studied. In the present paper the action of sulphurous acid on calcium permanganate has been discussed.

Experimental

N-Sulphurous acid, prepared as described in a previous communication (*loc. cit.*, 1955), was made to react with calcium permanganate solution (100 c.c., 1%), taken in two different beakers, exactly in the similar way, till the pink colour was just discharged (intermediate stage). The precipitate from the filtrate was found to contain calcium oxide, manganese oxide and manganese dioxide. Manganese dioxide was estimated by the method used by Mohammad and Ahluwalia (*ibid.*, 1941, **18**, 309). Total manganese content of the precipitate after separation from calcium (cf. Treadwell & Hall, "Analytical Chemistry", Vol. II, p. 205) was estimated as pyrophosphate (*ibid.*, p. 191) and manganese corresponding to manganese oxide content was calculated by subtraction. The calcium content of the precipitate was estimated as oxalate volumetrically. The composition of the compound formed was found to be as $CaO : 2\ MnO : 13\ MnO_2$. The various sulphur acids in the filtrate were estimated as before (*loc. cit.*), and calcium, as in the precipitate. The manganese content of the filtrate being too small for any quantitative estimation was determined by subtracting the amount of manganese present in the precipitate from the total added. Calcium in the filtrate was accounted for as SO_4^{2-} and $S_2O_6^{2-}$.

Further, experiments in duplicate were repeated with increasing volumes of normal sulphurous acid (decolorisation stage). The various products of reaction were estimated from the precipitates and the filtrates similarly, In the final stage, when the compound first formed completely dissolved, Mn was accounted for as SO_4^{2-} only, and Ca as SO_4^{2-} and $S_2O_6^{2-}$, both.

Again, the preliminary stage of the reaction was studied with insufficient amounts (three-fourth and half) of sulphurous acid required for the intermediate stage. Any unchanged permanganate was estimated by titrating against ferrous ammonium sulphate solution (A.R.). The various products of reaction are shown in Table I.

TABLE I

Various products of reaction when normal sulphurous acid reacts with calcium permanganate (100 c.c, 1%).

Total Ca added = 0.1089 g. Total Mn added = 0.2985 g.

Expt. No.	H_2SO_3 added. (c.c.)	$Ca(MnO_4)_2.5\,H_2O$. %Decomposition.	$CaSO_4$.	CaS_2O_6.	$MnSO_4$.	H_2SO_4.	CaO : MnO : MnO_2. Mol. ratio.	CaO : MnO : MnO_2. Mol. ratio (approx.)
1	10 00	46.83	0.1283 g.	0.0077 g.	0.0011 g.	0 3244 g.	1 : 1.55 : 7.84	1 : 2 : 8
	10.00	46.21	0.1282	0.0058	0.0027	0.3234	1 : 1.73 : 7.69	1 : 2 : 8
2	15.00	78.90	0.2475	0.0094	0.0019	0.4451	1 : 1.76 : 13.10	1 : 2 : 13
	15.00	78.41	0.2462	0.0100	0.0025	0.4492	1 : 1.84 : 13.05	1 : 2 : 13
3	19.55	100.00	0.2957	0.0315	0.0027	0.5925	1 : 1.70 : 12.66	1 : 2 : 13
	19.60	100.00	0.2989	0.0315	0 0047	0.5932	1 : 1.83 : 13.46	1 : 2 : 13
4	19.55	100.00	0.2979	0.0312	0 0055	0.5920	1 : 1 86 : 12.97	1 : 2 : 13
	19 45	100.00	0.2987	0.0294	0.0055	0.5925	1 : 1.76 : 12.58	1 : 2 : 13
5	22.00	100.00	0.2970	0.0570	0.1595	0.6000	1 : 3.85 : 14.65	1 : 4 : 15
	22.00	100.00	0.2966	0.0595	0.1570	0.6010	1 : 4.17 : 15.10	1 : 4 : 15
6	25.00	100.00	0.3012	0.0772	0.3244	0.6075	1 : 11.03 : 23.66	1 : 11 : 24
	25.00	100.00	0.2968	0.0782	0.3296	0.6056	1 : 11.00 : 24.10	1 : 11 : 24
7	32.00	100.00	0.2977	0.1068	0.8205	0.5692	Nil	Nil
	32.10	100.00	0.2965	0.1078	0.8205	0.5702		
8	SO_2 gas	100.00	...	...	...	...	1 : 1.90 : 13.30	1 : 2 : 13
		100.00	...	...	...	...	1 : 1.88 : 13 20	1 : 2 : 13

Finally the composition of the compound formed in the intermediate stage was ascertained by bubbling SO_2 gas through calcium permanganate solution (100 c.c., 1%) till the pink colour just disappeared.

DISCUSSION

In the intermediate stage 74.4% of SO_4^{2-} is present as H_2SO_4, 86.3% of Ca remains in the filtrate as SO_4^{2-} and $S_2O_6^{2-}$, and Mn mostly (99.4%) remains in the precipitate.

Calcium sulphate content increases in the preliminary stage and becomes maximum in the intermediate stage and remains afterwards unaltered. Manganese sulphate content increases regularly till in the final stage total Mn is accounted for as SO_4^{2-}. This may be due to the interaction of hydrated manganese dioxide and sulphurous acid. According to Meyer (*Ber.*, 1901, **34**, 3606) manganese dioxide reacts with sulphurous acid as

$$2\,MnO_2 + 3\,H_2SO_3 = Mn_2(SO_3)_3 + 3\,H_2O + O$$
$$Mn_2(SO_3)_3 = MnSO_3 + MnS_2O_6,$$
$$MnSO_3 + O = MnSO_4 \quad \ldots \quad \ldots \quad (1)$$

while according to Spring and Bourgeois (*Bull. Acad. Belg.*, 1878, **45**, 151 ; *Bull. soc. chim.*, 1886, *ii*, **46**, 151) the reaction is as

$$MnO_2 + 2\,H_2SO_3 = MnS_2O_6 + 2\,H_2O \text{ and}$$
$$MnO_2 + SO_2 = MnSO_4. \quad \ldots \quad \ldots \quad (2)$$

The decrease in the calcium oxide content and a corresponding increase in the calcium dithionate content suggest that manganese dithionate from reaction (1) or (2), perhaps, further reacts with calcium oxide as

$$CaO + MnS_2O_6 = CaS_2O_6 + MnO. \quad \ldots \quad \ldots \quad (3)$$

This manganese oxide immediately reacts with sulphuric acid as

$$MnO + H_2SO_4 = H_2O + MnSO_4. \quad \ldots \quad \ldots \quad (4)$$

which arrests the increase of sulphuric acid resulting from the oxidation of sulphurous acid by permanganate in the preliminary stage, and hydrated manganese dioxide afterwards reacts with H_2SO_3 as

$$MnO_2 + H_2SO_3 = H_2SO_4 + MnO. \quad \ldots \quad \ldots \quad (5)$$

Manganese oxide, thus formed, accumulates in the precipitate. The increase in the sulphuric acid content in the filtrate and manganese oxide content in the precipitate further suggest that in the presence of manganese dioxide, manganese oxide from reaction (5) does not undergo the reaction (4). Increase in the sulphuric acid content continues till manganese dioxide is just to be exhausted. In the final stage manganese dioxide is completely reduced to manganese oxide. Sulphuric acid then reacts with it and decreases suddenly. Then total Mn is accounted for as SO_4^{2-}, total Ca as SO_4^{2-} and $S_2O_6^{2-}$, both ; the reaction may be represented by the equation :

$$5\,Ca(MnO_4)_2 + 26\,H_2SO_3 = 4\,CaSO_4 + 10\,MnSO_4 + CaS_2O_6 + 10\,H_2SO_4 + 16\,H_2O \quad (6)$$

The composition of the precipitate, formed in the intermediate stage by adding sulphurous acid or bubbling SO_2 gas, is identical *i.e.* CaO.2 MnO.13 MnO_2. In expt. No. 1 (Table I) the compound formed is CaO.2 MnO.8 MnO_2, while in expt. No. 2 it is the same as in the intermediate stage. Since after the intermediate stage manganese dioxide and calcium oxide contents decrease whereas manganese oxide content increases, the ratio CaO : MnO : MnO_2 changes to 1: 4 : 15 and 1: 11 : 24 respectively in the later experiments (5 & 6, Table I).

Due to the very weak acidic properties of hydrated manganese dioxide a polypermanganous acid, *i.e.* $H_2Mn_2O_5$, is perhaps formed in the preliminary stage of the reaction. This acid may further be responsible for the formation of higher polypermanganites (Cocosinscy, *Z. anorg. Chem.*, 1930, **176**, 186; 1930, **293**, 189).

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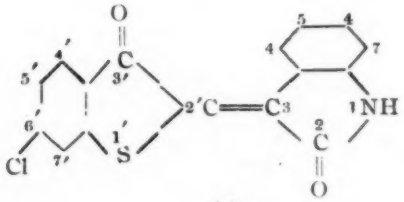
INDIGOID VAT DYES OF THE ISATINSERIES. PART VIII. 3-INDOLE-2′-(6′-CHLORO)-THIONAPHTHENE-INDIGOS

By Sisir Kumar Guha and Jnanendra Nath Chatterjea

6-Chloro-3-hydroxythionaphthene has been condensed with isatin and some of its substituted products. The thioindigoid dyes of this series have been found lighter in colour than those of the corresponding compounds of the 5-chloro- and 7′-chloro- series studied already. A very pure specimen of the intermediate 5-chlorophenylthioglycollic acid-2-carboxylic acid was obtained in 64% yield

3-Indole-2′-(6′-chloro)-thionaphthene-indigos have now been prepared for the comparison of their colour and dyeing shades with those of the isomeric 5′-chloro- and 7′-chloro-thionaphthene-indigos, already studied (Guha and Basu-Mallick, this *Journal*, 1946, **23**, 214 ; Guha and Chatterjea, *ibid.*, 1947, **24**, 473). Here 6-chloro-3-hydroxy-thionaphthene (Friedländer and Sander, *Ber.*, 1924, **57**, 648) was condensed with isatin and some of its substituted products. Thus, another series of asymmetrical thioindigoid dyes of the general formula (I) has been obtained.



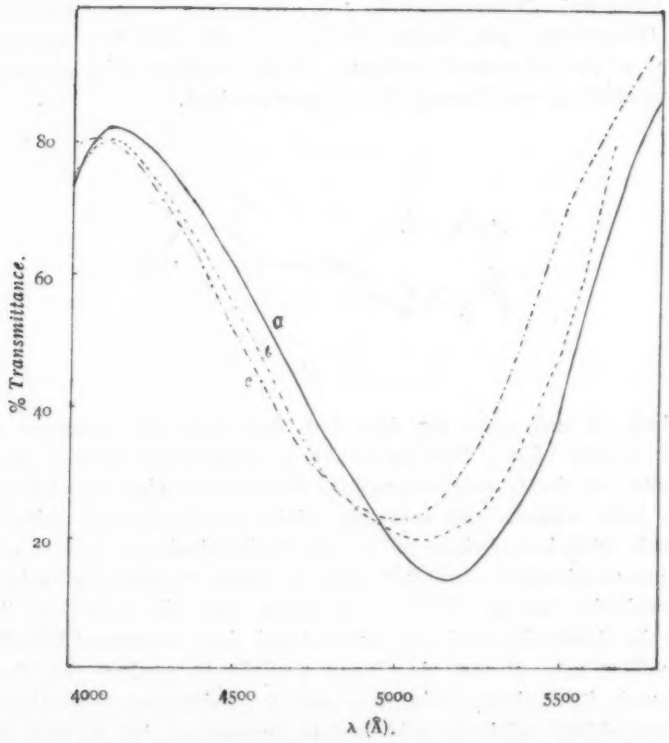
(I)

The products of this series are dark red, deep red and violet-red crystalline dyes obtained in 88-97% yield. They are soluble in nitrobenzene, aniline, pyridine and tetralin, difficultly soluble in xylene except the dibromo compound which is moderately soluble in the same solvent, and sparingly soluble in alcohol and carbon tetrachloride. They melt when heated above 320°. The dyeing shades of all these compounds, excepting the parent substance, were fully and uniformly developed on cotton from an alkaline hydrosulphite vat at 55°-60°. In every case, the colour of the vat is yellow except the dinitro dye and the symmetrical dye, mentioned hereafter, which give a deep yellow vat. It was also found possible to produce the shade of the mother compound, its 5-chloro, 5-bromo, and 5 : 7-dibromo derivatives on wool uniformly from a dilute sulphuric acid bath in suspension, but no such shade could be developed on wool in the same way from the bromonitro and the dinitro compounds.

A study of the colour, dyed shades and absorption curves of the pure dyes (Figs. 1-3) of 6′-chloro- series together with those of the corresponding compounds of 5′-chloro- and 7′-chloro-series (*loc. cit.*), reveals clearly that the change in colour due to the influence of the chlorine atom in 5′-, 6′- and 7′- positions of the thionaphthene ring of 3-indole-2′-thionaphthene-indigos is in the order: 5′chloro > 7′-chloro > 6′-chloro compounds (Table I).

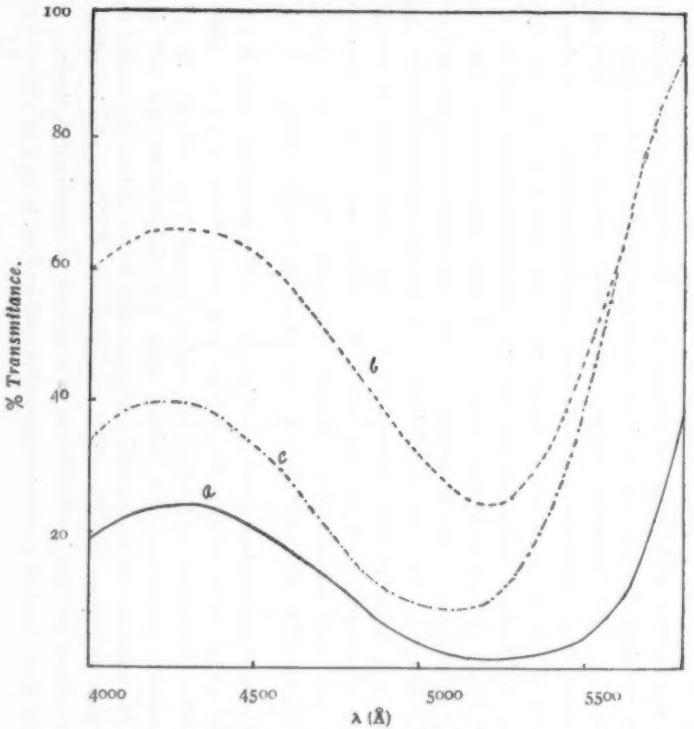
The symmetrical dye, 6 : 6′-dichlorothioindigo (Ciba Red B) has been described as a dark red powder (E. P. 6490/07 ; U. S. P. 848354 ; Friedländer and Sander, *loc. cit*). This has now been obtained in violet-red crystals, not melting below 320°, by the oxidation of a pure specimen of 6-chloro-3-hydroxythionaphthene (vide Experimental, methods I & II). The intermediate 5-chlorophenylthioglycollic acid-2-carboxylic acid was obtained from 4-chloroanthranilic acid (Hunn, *J. Amer. Chem. Soc.*, 1923, **45**, 1024) by standard methods and was obtained in a high state of purity in 64% yield.

FIG. 1



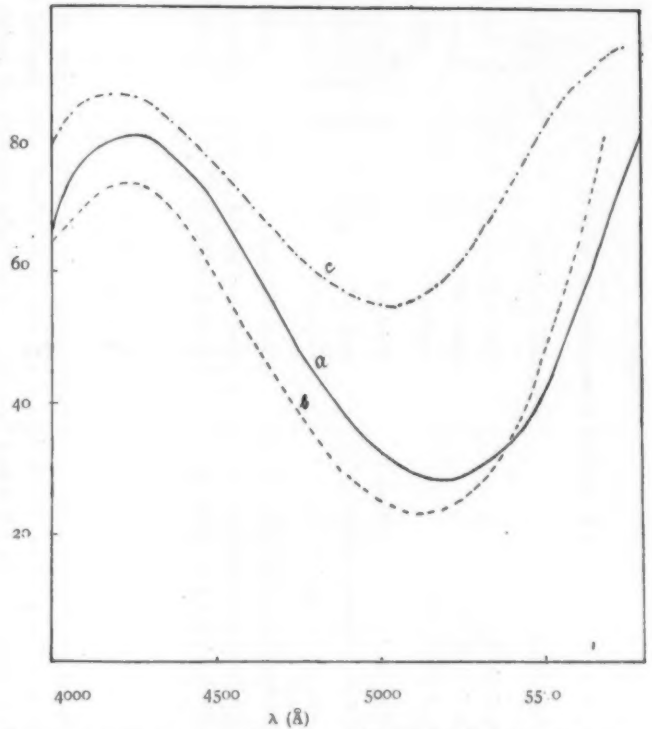
Curves *a-c* represent respectively 3-indole-2′-(5′-chloro-, 7′-chloro-, and 6′-chloro)-thionaphthene-indigo.

FIG. 3



Curves *a-c* represent respectively 3-(5 :7-dinitro)-indole-2′-(5′-chloro-, 7′-chloro- and 6-chloro)-thionaphthene-indigo.

FIG. 2



Curves *a-c* represent respectively 3-(5 :7-dibromo)-indole [2′-(5′-chloro)-, 2′-(7′-chloro)- and 2′-(6′-chloro)]-thionaphthene-indigo.

TABLE I

[T denotes thionaphthene-indigo]

Compounds.	Dyed shade on cotton.	Absorption maxima.
3-Indole-2′-(5′chloro)-T	Deep red	5150 Å
3-Indole-2′-(6′-chloro)-T	Light red	5000
3-Indole-2′-(7′-chloro)-T	Darkish red	5060
3-(5 :7-Dibromo)indole-2′-(5′-chloro)-T	Violet-red	5200
3-(5 :7-Dibromo)indole-2′-(6′-chloro)-T	Deep red	5030
3-(5 :7-Dibromo)indole-2′-(7′-chloro)-T	Violet-red	5110
3-(5 :7-Dinitro)indole-2′-(5′-chloro)-T	Deep violet-red	5250
3-(5 :7-Dinitro)indole-2′-(6′-chloro)-T	Darkish violet-red	5100
3-(5 :7-Dinitro)indole 2′-(7′-chloro)-T	Darkish violet-red	5220

EXPERIMENTAL

5-Chlorophenylthioglycollic acid-2-carboxylic Acid.—The solution of 4-chloroanthranilic acid (17.2 g.) in NaOH (100 c. c., 4%) was added with stirring to a solution of HCl (conc., 30 c.c.) in water (300 c.c.). The finely precipitated amine was then diazotised at 0°-5° by a solution of sodium nitrite (70 c. c., 10%). The opalescent solution was added with constant stirring to a previously cooled solution of ethyl potassium xanthate (20 g.) and sodium carbonate (40 g.) in water (300 c. c.) containing ice (100 g.). The resulting yellow precipitate, which was continually stirred till the room temperature (28°) was attained, turned into a brownish yellow liquid. A solution of NaOH (25 g. in 50 c. c. water) was then added to the oily mixture and heated in the boiling water-bath for 3 hours. Monochloroacetic acid (20 g.), neutralised with dilute sodium carbonate, was poured into the mixture which was heated further for 45 minutes. The yellowish solution was cooled and acidified with a little excess HCl (dilute). The fine precipitate of 5-chlorophenylthioglycollic acid-2-carboxylic acid was collected and crystallised from hot water (norite) in nearly colorless prisms, m. p. 216-17°, yield 16-18 g. (D. R. P. 193724 and E. P. 6490/07 record m. p. 190°-95° and 194° respectively). (Found: C, 43.5; H, 3.0; Cl, 5.0; S, 13.3. Calc. for $C_9H_7O_4ClS$: C, 43.8; H, 2.9; Cl, 14.4; S, 13.0 per cent).

6-Chloro-3-hydroxythionaphthene : Method I.—The foregoing acid (3 g.) was powdered and added with stirring to NaOH (12 g.) and water (1.2 c. c.) contained in a wide-mouthed hard glass test tube and heated between 170° and 180° for 1 hour with constant stirring on a sand-bath, taking care that the mixture did not dry up and remelt. The mixture was cooled and extracted with warm water; the cooled extract was acidified with HCl (conc.). The crude precipitate of 6-chloro-3-hydroxythionaphthene was collected and purified by distillation in a current of superheated steam. The colorless leaflets were dried in a vacuum desiccator and had m. p. 143-45°, yield 1.3 g. (59%).

TABLE II

[T denotes thionaphthene-indigo. C denotes 6-chloro-3-hydroxythionaphthene]

Name of dye.	Mol. formula.	Constituents.	Glacial acetic acid used and appearance	Yield.	Solubility.	Dyed shade on cotton.	Analysis Found.	Analysis Calc.
3-Indole-2′-(6′-chloro)-T	$C_{16}H_8O_2NClS$	Isatin (0.59 g.) +C (0.74 g.)	40 c.c. Fine shining dark red needles	1.16 g. (92%)	Moderately in acetone; sparingly in benzene.	Light red	C :60.8 % H : 2.6 N : 4.4	61.2 % 2.5 4.6
3-(5-Chloro)-indole-2′-(6′-chloro)-T	$C_{16}H_7O_2NCl_2S$	5-Chloroisatin (0.55 g.)+ C (0.55 g.)	50 c.c. Long lustrous dark red rectangles	1.01 g. (97%)	Moderately in acetone and benzene	Darkish red	N : 4.2	4.02
3-(5-Bromo)-indole-2′-(6′-chloro)-T	$C_{16}H_7O_2NClBrS$	5-Bromoisatin (0.68 g.)+ C (0.55 g.)	45 c.c. Fibre-like dark red long needles	1.05 g. (89%)	Do	Do	N : 3.8	3.56
3-(5 :7-Dibromo)-indole-2′-(6′-chloro)-T	$C_{16}H_6O_2NClBr_2S$	5 :7-Dibromo-isatin(0.58 g.) +C (0.35 g.)	30 c.c. Fibre-like deep red small needles	0.84 g. (94%)	Sparingly in acetone and benzene.	Deep red	N : 3.2	2.96
3-(5-Bromo-7-nitro)-indole-2′-(6′-chloro)-T	$C_{16}H_6O_4N_2ClBrS$	5-Bromo-7-nitroisatin (0.81 g.)+ C (0.55 g.)	50 c.c. Shining violet-red rectangles	1.22 g. (93%)	Moderately in benzene and sparingly in acetone.	Brownish red	C : 43.4 H : 1.2 N : 6.7	43.9 1.4 6.4
3-(5 :7-Dinitro)-indole-2′-(6′-chloro)-T	$C_{16}H_6O_6N_2ClS$	5 :7-Dinitro-isatin (0.55 g.) +C (0.43 g.)	80 c.c. Fine long violet-red needles	0.83 g. (88%)	Moderately in acetone and benzene; slightly in chloroform.	Dark violet red	N : 10.5	10.4
6 :6′-Dichloro-thioindigo	$C_{16}H_6O_2Cl_2S_2$	C (1.0 g.) in dil. NaOH (50 c.c.) oxidised by $K_3Fe(CN)_6$ soln. (5%)	Lustrous violet-red needles	0.91 g. (92%	Difficultly in nitrobenzene and tetralin; moderately in pyridine; sparingly in benzene, toluene and xylene	Violet-red	S : 17.2 Cl : 19.0	17.5 19.4

Method II.—A mixture of the thioglycollic acid (5 g.), freshly fused sodium acetate (5 g.) and acetic anhydride (20 c. c.) was boiled under reflux for 2 hours. The solution turned from red to slight yellow. It was cooled and the mixture treated with water. The oily residue was boiled with an excess of 2 *N*-NaOH for ½ hour. The resulting solution, on acidification, afforded the crude hydroxythionaphthene which was purified as in Method I, m. p. 143-45°, yield 2 g. (54%). (Friedländer and Sander, *loc. cit.*, record m. p. 143°).

3-Indole-2′-(6′-chloro)thionaphthene-indigos, recorded in Table II, were prepared from equimolecular quantities of the constituents in glacial acetic acid in the presence of HCl (conc., 3-4 c. c.) by boiling for ½ hour. They were all crystallised from nitrobenzene, washed with alcohol and hot water and dried at 110°. The crystallised sample invariably appeared darker in colour than the crude condensed product.

One of the authors (S. K. G.) wishes to express his thanks due to Dr. S. K. Mukherjee, D. Sc. and Dr. Monisha Bose, M. Sc., D. Phil. of the University College of Science and Technology, Calcutta, for kindly helping with spectrophotometric measurements.

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USE OF DIPHENYLTHIOVIOLURIC ACID AS A REAGENT FOR GRAVIMETRIC ESTIMATION OF METALS. PART I. ESTIMATION OF COPPER

By R. P. Singh and Vishnu Shankar

Diphenylthioviolurie acid has been found to be a suitable reagent for the gravimetric estimation of coppe'. The metal was precipitated quantitatively from its salt solutions by aqueous solutions of the ammonium salt of diphenylthioviolurie acid. p^H of the solution must be within certain limits, otherwise quantitative precipitation does not take place.

Numerous organic reagents have been tried for the gravimetric estimation of copper during the last fifty years. Of these, α-benzoin-oxime, quinaldinic acid, salicylaldoxime etc. have been found to yield quantitative results.

In a previous communication (Gambhir and Singh, *Proc. Ind. Acad. Sci.*, 1946, **23A**, 330), the preparation of a number of complex compounds of diphenylthioviolurie acid with metals was reported. In the case of copper, a brown complex was obtained in the form of a precipitate on adding an aqueous solution of the ammonium salt of diphenylthioviolurie acid to a copper salt solution.

Experimental

Ammonium Salt of Diphenylthioviolurie Acid.—Diphenylthiobarbituric acid was obtained by condensing a mixture of diphenylthiourea and malonic acid in presence of acetyl chloride. It was then converted into diphenylthioviolurie acid by adding sodium nitrite, followed by addition of dilute sulphuric acid. The acid thus obtained was converted into the ammonium salt by addition of an excess of dilute ammonia (in which it dissolves) with constant stirring. The excess of ammonia was removed by evaporating the solution on a water-bath. By evaporation to dryness, the solid salt was left behind.

Estimation of Copper.—Standard solutions of copper were prepared by dissolving copper sulphate (A.R., B.D.H.). The purity of the sample was tested by iodimetric titration and was found to be 99.8%.

Estimations of copper in nearly neutral solutions, without adjusting the p_H, showed that precipitations were not quantitative. An attempt was then made to ascertain the effect of the change in p_H on precipitation in this case. On investigation it was found that the results were fairly accurate if the estimations were carried out between the p_H range of 7.2 and 8.0 This is shown by observations recorded in the table below. The following procedure was adopted for these estimations.

A freshly prepared solution (10 c.c.) of copper sulphate (Cu content 0.07 g. approx.) was diluted to about 35 c.c., acidified with H_2SO_4 (dil., 2-3 c.c.) and then made alkaline with a dilute solution of ammonia till p_H between 7.2 and 8.0. p_H of the solutions was measured in a potentiometer using a quinhydrone electrode. The solution was heated to 85° and the reagent solution was added slowly until the precipitation was quantitative

i.e. the filtrate gave no test for copper. This required about three times the calculated quantity of the ammonium salt. The precipitate was boiled for 2 to 3 minutes, removed from the flame and kept for about half an hour. It was then filtered through a sintered glass crucible No. 3 under gentle suction. The precipitate was washed thoroughly with hot distilled water and finally dried at 110° in a constant temperature air oven or in a desiccator over fused calcium chloride. The results of the estimations carried out by this method are shown in Table I.

TABLE I

Vol. of Cu soln. for each estimation = 10 c.c. Ammonium salt soln. = 0.8%.
Ammonium compound added = 220 c c.

No.	p_H.	Weight of copper in solution. Found.	Calc.	% Error.
1	8.0	0.0743 g.	0 0740 g.	0.39
2	7.7	0 0740	0.0740	0.239
3	7 5	0 0740	0 0740	0.367
4	7.2	0.0738	0.0740	0.320
5	7.7	0.0572	0.0574	0.209
6	7 5	0.0571	0.0574	0.383

Estimation of copper can thus be carried out accurately by this reagent between the p_H range of 7.2 and 8.0. An attempt is being made to estimate copper by this reagent in presence of other metals.

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REACTION OF HYPONITRITES. PART IV. CHEMICAL ESTIMATION OF SODIUM HYPONITRITE, SODIUM NITRITE AND SODIUM NITRATE IN PRESENCE OF EACH OTHER

By T. M. Oza and N. L. Dipali

Nitrite and nitrate have been estimated in the mixture of the three sodium salts, nitrite, nitrate and hyponitrite, after exposing the mixture to the action of carbon dioxide. Hyponitrite can also be destroyed by boiling a solution of the three salts without affecting the nitrite and nitrate content. The mixture is treated with silver nitrate, the precipitated silver nitrite is washed off from the mixed precipitate of silver nitrite and silver hyponitrite and the silver hyponitrite treated with standard sulphocyanide after dissolving in dil HNO_3. The nitrite in the filtrate is estimated by the usual method. For estimating nitrate, either hyponitrite alone is decomposed by boiling the solution or both hyponitrite and nitrite are decomposed by treatment with 7 *N*-H_2SO_4. The solution containing the hyponitrite can be preserved only in strongly alkaline state.

Partington and Shah (*J. Chem. Soc.*, 1931, 2071; 1932, 2589) estimated the purity of hyponitrites by measuring nitrogen with the Dumas method. Oza and Walawalker (this *Journal, Ind. & News Ed.*, 1945, **9**, 57) showed that sodium hyponitrite solution was fairly stable in a strongly alkaline medium and that it could be titrated with standard sulphocyanide after precipitation as silver salt. Oza, Dipali and Walawalker (*J. Univ. Bom.*, 1945, **14**, No. 3, p. 27) have shown that nitrate in admixture with hyponitrite can be estimated after decomposing the latter with 7*N*-H_2SO_4. Oza, Oza and Dipali (this *Journal*, 1951, **28**, 15) showed also that hyponitrites in solution (or suspension) were decomposed completely on boiling, and nitrite in admixture could therefore be estimated.

In the present paper the possibility of chemical estimation of sodium hyponitrite, nitrite and nitrate in admixture has been studied. The action of carbon dioxide on sodium hyponitrite in (*i*) a dry system and (*ii*) a system not carefully dried, has been studied and the results applied to the estimation of nitrite and nitrate present in admixture.

Experimental

Sodium hyponitrite was prepared according to Oza (this *Journal*, 1945, **22**, 225). Sodium nitrite and sodium nitrate were recrystallied and tested specimens of the pure salts, dried and kept in desiccators.

Experiments were first carried out to test the effect of carbon dioxide on sodium hyponitrite in evacuated systems. Weighed quantity of the salt was kept in a bulb exposed to P_2O_5 in the system for one day and dry carbon dioxide was then introduced. The results in Table I show that very dry sodium hyponitrite is very negligibly affected by carbon dioxide. All volumes of gas are at N.T.P.

TABLE I

Effect of dry carbon dioxide on dry sodium hyponitrite

$Na_2N_2O_2$ taken (g.)	0.0190	0.0732
Gas released (c.c.)	0.35	0.43

When, however, the salt was not carefully dried, and exposed to carbon dioxide in the system, the results recorded in Table II were obtained.

TABLE II

Effect of carbon dioxide on sodium hyponitrite in vacuo.

1 $Na_2N_2O_2$ taken.	2 Gas given off.	3 $Na_2N_2O_2$ calc. from (2).	4 c.1064*N*-H_2SO_4 reqd. by residue.	5 $Na_2N_2O_2$ calc. from (4).
0.0192 g.	4.1 c.c.	0.0194	3.65 c.c.	0.0189
0.0254	5.2	0.0247	4.50	0.0254
0.0288	6.1	0.0288	5.05	0.0285
0.0312	6.7	0.0318	5.65	0.0318

Column (3) records $Na_2N_2O_2$ calculated as

$$Na_2N_2O_2 + CO_2 = Na_2CO_3 + N_2O$$

on the assumption that the gas is all nitrous oxide (Oza, this *Journal*, 1944, **21**, 71); column (4) records titration results of the residue and column (5), $Na_2N_2O_2$ calculated therefrom (Oza, Dipali and Oza, *ibid.*, 1950, **27**, 499).

Experiments were performed on exposing mixtures of sodium hyponitrite and sodium nitrite in vacuo as well as in air to carbon dioxide yielding results shown in Table III.

TABLE III

Effect of carbon dioxide on mixtures of $Na_2N_2O_2$ *and* $NaNO_2$ *in air* (10 *mins.*).

Mass in mixture. $Na_2N_2O_2$.	$NaNO_2$.	$KMnO_4$ (0.0985*N*) reqd by residue.	$NaNO_2$ calc from $KMnO_4$ consumed.
0.0240 g.	0.0242 g.	7.4 c.c.	0.0252 g.
0.0212	0.0176	5.3	0.0179
0.0170	0.0132	4.15	0.0141
0.0160	0.0324	9.60	0.0326
0.0164	0.0182	5.15	0.0189
0.0228	0.0420	12.45	0.0423

The results show that the nitrite can be accurately estimated in this way. In these experiments the mixture was kept at the bottom of the conical flask and carbon dioxide released through a tube so as to be let out just above the powder.

The experiments were done next with the hyponitrite and nitrite in solution, and carbon dioxide was bubbled through t'c solution. The results in Table IV show that the hyponitrite is not all decomposed and some of it, left over, contributes to the permanganate consumed. Oza and Walawalker (*loc. cit.*) and Partington and Shah (*loc cit.*) and others showed that permanganate was consumed by the hyponitrite.

TABLE IV

Effect of bubbling carbon dioxide into a solution of a mixture of $Na_2N_2O_2$ *and* $NaNO_2$.

$Na_2N_2O_2$ taken.	$NaNO_2$ taken.	$NaNO_2$ found.
0.0326 g.	0.0402 g.	0.0498 g.
0.0360	0.0208	0.0272
0 0316	0.0472	0.0512
0.0248	0.0538	0.0665
0.0210	0.0290	0 0393

In solution, however, the hyponitrite is completely decomposed on boiling, without affecting the nitrite, and the nitrite left can therefore be satisfactorily estimated in this way. Results in Table V show that the method is satisfactory.

TABLE V

Titration of $NaNO_2$ *with* $KMnO_4$ *after boiling the solution of mixtures containing* $Na_2N_2O_2$ *and* $NaNO_2$.

$Na_2N_2O_2$ taken.	$NaNO_2$ taken.	$KMnO_4$ reqd.		$NaNO_2$ calc. from $KMnO_4$ consumed.
0.0382 g.	0.0398 g.	11 30 c c.	0.1007*N*	0.0393 g.
0.0356	0.0519	14.75		0 0512
0.0288	0.0469	13.25		0.0460
0.0246	0 0259	7.80	0 0987*N*	0.0265
0.0144	0 0313	9.05		0 0308
0.0206	0.0286	8.40		0.0286
0 0208	0 0232	6.90	0.0390*N*	0 0235
0.0226	0.0293	8.85		0.0303
0.0224	0 0265	7 60		0.0260

To estimate the amount of hyponitrite in such mixtures, the precipitation method can also be applied. Silver nitrite is fairly soluble in water at room temperature and it can be removed, by washing, from the mixed precipitate of silver nitrite and silver hyponitrite. The washing is done till the filtrate ceases to respond to the test for nitrite, the washings being collected and added to the first filtrate for subsequent estimation of the contained nitrite. The precipitate is then dissolved in dilute HNO_3 and titrated with standard sulphocyanide. The results are shown in Table VI. If the mixture contains very large amounts of nitrite, errors are appreciable as appreciable silver hyponitrite passes into solution in the large number of washings then required.

TABLE VI

Estimation of $Na_2N_2O_2$ *in admixture with* $NaNO_2$ *after precipitation as* $Ag_2N_2O_2$.

$Na_2N_2O_2$ taken.	$NaNO_2$ taken.	KCNS reqd. (0.01476 *N*)	$Na_2N_2O_2$ calc.
0.0286 g.	0.0505 g.	12.25 c.c.	0.0290 g.
0.0204	0.0196	8.35	0.0197
0.0133	0.0142	5 30	0.0126
0.0244	0.0397	10 35	0.0245
0.0212	0 0388	9.10	0 0216
0.0221	0 0718	9.25	0 0220

The method of precipitation, shown above, becomes applicable to mixtures of hyponitrite, nitrite and nitrate as well, provided that the quantities of nitrite are not very large. In a portion of the solution nitrite and hyponitrite are precipitated at a low temperature, the mixed precipitate is washed free of silver nitrite and the insoluble hyponitrite titrated out. Nitrite is estimated in the filtrate to which all the washings are added. For determining nitrate, a measured volume of the solution is boiled to decompose the hyponitrite and the nitrite is oxidised to nitrate and the total nitrate is then estimated; nitrate equivalent of nitrite is then subtracted from total nitrate to obtain nitrate. Table VII records results obtained in this way.

TABLE VII

Estimation of $Na_2N_2O_2$, $NaNO_2$ and $NaNO_3$ *in a mixture.*

$Na_2N_2O_2$ taken	$NaNO_2$ taken	$NaNO_3$ taken.	$Na_2N_2O_2$ found.	$NaNO_2$ found.	$NaNO_3$ found.
0.0526 g.	0.0436 g.	0.0308 g.	0.0508 g.	0.0447 g.	0.0298 g.
0.0234	0.0243	0.0616	0.0236	0.0238	0.0608
0.0388	0.0842	0.0246	0 0378	0.0843	0.0256
0.0472	0.0476	0.0492	0.0456	0 0475	0.0478

If the solutions are allowed to stand for some time before the estimation is commenced, the hyponitrite present therein must be stabilised by making the solution strongly alkaline (Oza and Walawalker, *loc. cit.*).

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PREPARATION OF 5-AMINO-2-ARYLIMINO-4-THIAZOLIDONES

By Birendra Kumar Patnaik and M. K. Rout

Nine 5-aminothiazolidones have been prepared by fission of the corresponding azo derivatives. Reasons for placing the azo group in 5-position of the thiazolidone nucleus in the azo derivatives have been discussed.

In view of the thiazolidones exhibiting a wide range of different activities, it appeared to us of interest to prepare some amino derivatives of this class of compounds with amino group attached directly to the thiazolidone nucleus. Such structural feature is considered to prove highly advantageous, as it can provide routes to the synthesis of several related compounds of great biological and therapeutic interest.

Thiazolidones, in the present investigation, were prepared by a method already reported (Pujari and Rout, this *Journal*, 1954, **31**, 701 ; Das and Rout, *J. Sci. Ind. Res.*, 1955, **14B**, 16). These were then coupled with diazotised aniline in alkaline medium. Bogert and Cherbcoff (*J. Amer. Chem. Soc.*, 1924, **46**, 2864) observed that 2-aminothiazole coupled with diazotised *p*-nitroaniline or sulphanilic acid, the point of attachment being at the 5-position of the thiazole nucleus. Ganapati and Venkataraman (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 348) and Beyer and Wolter (*Chem. Ber.*, 1952, **83**, 85, 1077) have also confirmed the above observation.

The close relationship between thiazoles and thiazolidones suggests that the azo group is linked to the thiazolidone nucleus in the position corresponding to that at which coupling takes place on the thiazole nucleus.

Further evidences supporting the above view were drawn from the work of Meerwien, Büchner and Engster (*J. prakt. Chem.*, 1939, **152**, 237) who from the reactions of diazonium salts with unsaturated carbonyl compounds demonstrated that the aryl-azo group entered the position α to the activating group. This was also supported by the work of Kvalnes (*J. Amer. Chem. Soc.*, 1934, **56**, 2478) and Freund (*J. Chem. Soc.*, 1951, 1943) who utilised this reaction in preparing 2-aryl-1 : 4-benzoquinones and 3-(*p*-arsonophenyl) coumarin. In thiazolidones, the CH_2 group in 5-position is in α-position to the activating carbonyl group ; hence the location of the azo group in 5-position is justified. A more definite and rigorous evidence leading to the same conclusion is that 5:5′-dimethylthiazolidone, in which the CH_2 group is blocked by methyl groups, does not couple with diazotised aniline.

2-Aryliminothiazolidones and their corresponding 5-azo derivatives are described in Table I. By cleavage of the azo group in the manner described in the Experimental, the corresponding amino compounds were prepared (Table II).

EXPERIMENTAL

5-Phenylazo-2-phenylimino-4-thiazolidone.—HCl (conc., 1.5-2 c.c.) was added to aniline (1 g.) and the mixture was warmed till the latter dissolved. The solution was rapidly chilled by adding crushed ice (4.5 g.) and stirred. The hydrochloride, placed in an ice-bath, was then diazotised by adding, during 10 minutes, an ice-cold solution of sodium nitrite (0.8 g. in 5-7 c.c. of water) slowly with stirring. An alkaline solution of 2-phenylimino-4-thiazolidone was prepared by dissolving the thiazolidone in a moderately concentrated solution of caustic soda and small amount of alcohol, and the solution was cooled in an ice-bath. The diazotised aniline was then added slowly with stirring to the ice-cold alkaline solution of the thiazolidone. After addition, the mixture was allowed to stand in the ice-bath, with stirring, for about two hours, after which it was acidified with 8-*N* acetic acid. The precipitate was collected, washed with cold water and finally recrystallised from alcohol, m.p. 133°, yield 65%. (Found: N, 18.3 ; S, 10.4. $C_{15}H_{12}ON_4S$ requires N, 18.91; S, 10.81 per cent).

5-Amino-2-phenylimino 4-thiazolidone.—The azo compound (approx. 1 g., prepared as described above) was dissolved in rectified spirit by heating. To this a solution of sodium hydrosulphite (3.5 g. in 10-20 c.c. of water) was added and the mixture refluxed till the colour of the solution nearly disappeared. More sodium hydrosulphite was added, if the colour did not fade within 10 to 15 minutes, and the refluxing was continued for 20 minutes more. The liquid was then filtered hot and the filtrate was concentrated on a wire-gauge which resulted in the separation of the compound. The product was extracted with enough hot water to dissolve any sodium hydrosulphite that came down along with the compound. The residue was collected, washed with cold water and finally recrystallised from alcohol, m.p. 74°, yield 45%. (Found: N, 19.95 ; S, 15.32. $C_9H_9ON_3S$ requires N, 20.28; S, 15.45 per cent).

TABLE I

	A. 2-Arylimino-4-thiazolidones.				B. 5-Phenylazo-2-arylimino-4-thiazolidones.			
Nature of aryl group.	M.P.	Yield.	% Sulphur.		M.P.	Yield.	% Sulphur.	
			Found.	Calc			Found.	Calc.
Phenyl	179°	80 %	16.26	16.66	133°	65 %	10.44	10.81
p-Tolyl	180°	80	15.08	15.53	152°	60	10.11	10.32
m-Chlorophenyl	176°	65	13.84	14.12	116°	50	9.16	9.65
p-Chlorophenyl	200°	75	13.72	14.12	136°	55	9.54	9.68
m-Nitrophenyl	133°	70	13.23	13.50	74°	55	8.98	9.38
p-Nitrophenyl	236°	85	12.92	13.50	*	65	9.21	9.38
p-Carboxyphenyl	>300°	60	13.31	13.55	167°	45	9.13	9.41
α-Naphthyl	184°	70	13.02	13.22	75°	55	8.87	9.24
β-Naphthyl	207°	65	12.86	13.22	57°	50	9.02	9.24

* Did not melt.

TABLE II

5-Amino-2-arylmino-4-thiazolidone.

Nature of aryl group.	M.P.	Yield.	% Nitrogen.		% Sulphur.	
			Found.	Calc.	Found.	Calc.
Phenyl	74°	45 %	19 45	20.28	15.32	15.45
p-Tolyl	93°	35	18.75	19.00	14.12	14.47
m-Chlorophenyl	89°	40	17.23	17.30	12.82	13.25
p-Chlorophenyl	94°	35	17.12	17.30	12.91	13.25
m-Nitrophenyl	167°	40	21.63	22.22	12.45	12.69
p-Nitrophenyl	85°	50	21.95	22.22	12.26	12.69
p-Carboxyphenyl	119°	45	16.15	16.73	12.52	12.75
α-Naphthyl	130°	30	16.22	16.34	12.15	12.45
β-Naphthyl	187°	35	15.93	16 34	11.88	12.45

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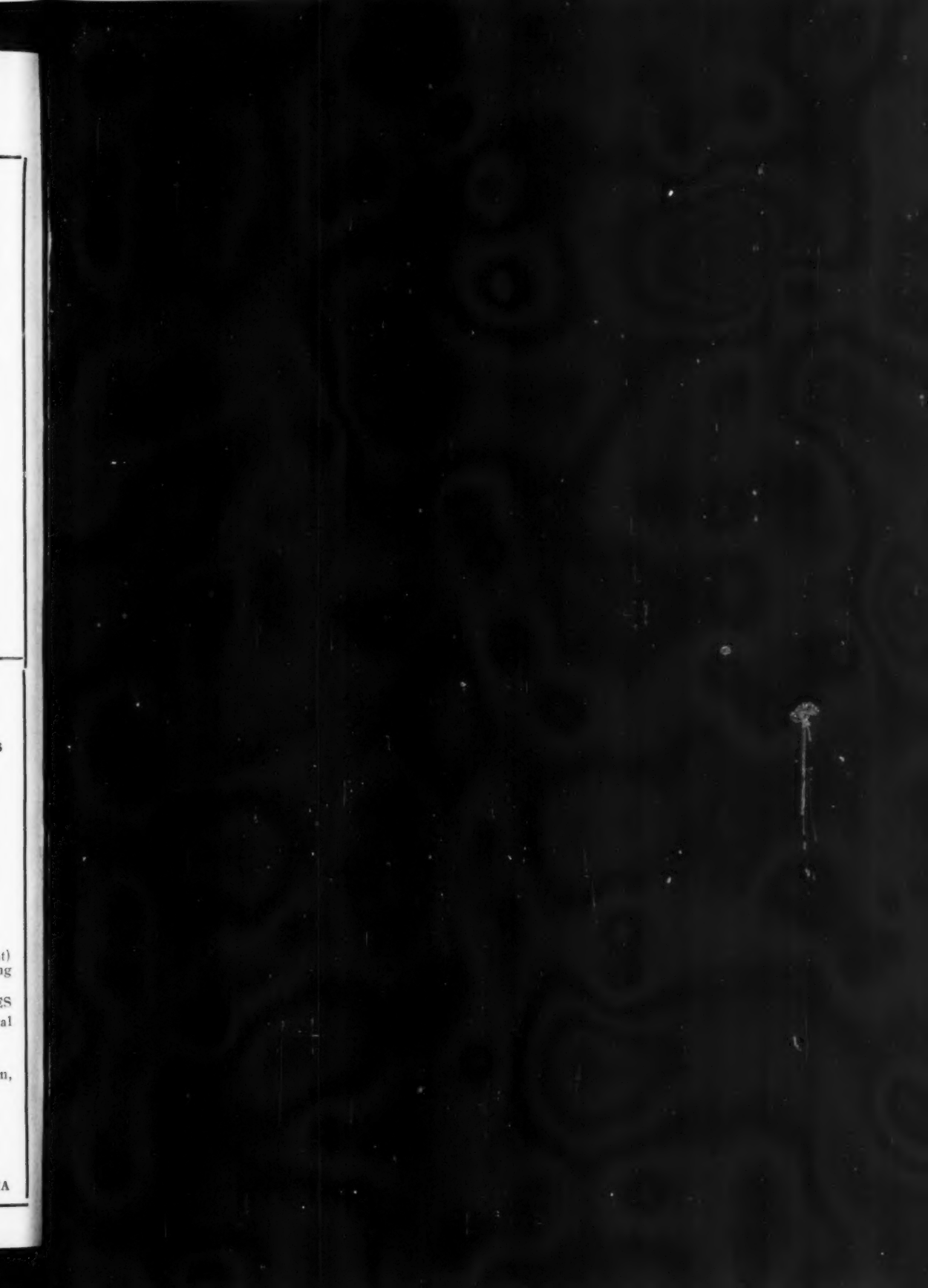

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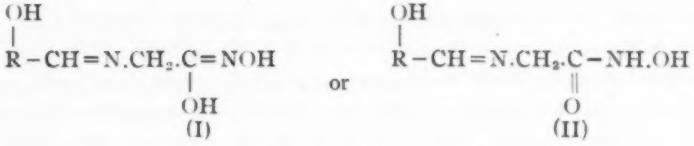
[Jour. Indian Chem. Soc , Vol. 32, No. 9, 1955]

INNER-METALLIC COMPLEX SALTS OF HYDROXYALDIMINO-HYDROXAMIC ACIDS WITH POLYCYCLIC RINGS. PART I

By Ajit Kumar Mukherjee and Priyadaranjan Rây

A number of complex compounds of bivalent copper, nickel, cobalt, and of sexivalent uranium with salicylaldehyde, resorcylaldehyde or β-hydroxynaphthaldehyde, and glycine-hydroxamic acid have been prepared and their properties studied. The Schiff's bases formed by the condensation of *o*-hydroxyaldehyde and glycine-hydroxamic acid behave as tridentate ligands. The structures of these metal chelates have been elucidated from a study of their magnetic properties.

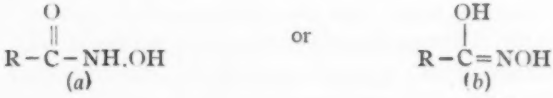
In previous papers (Mukherjee and Rây, this *Journal*, 1950, **27**, 707; 1955, **32**, 493) polycyclic inner-metallic complexes of copper, nickel, cobalt, manganese, iron, uranium and vanadium with different hydroxyaldimino acids have been described. The *o*-hydroxyaldehyde molecules in those complexes are believed to undergo condensation with different amino-acids giving rise to what may be termed as 'hydroxyaldimine acids' which function both as tridentate and bidentate units under suitable conditions. In continuation thereof we have now succeeded in preparing a number of similar metal chelate complexes of copper, nickel, cobalt and uranium with Schiff's bases derived from salicylaldehyde, resorcylaldehyde, or β-hydroxy-α-naphthaldehyde, and glycine-hydroxamic acid. Glycine-hydroxamic acid undergoes condensation with *o*-hydroxyaldehydes to form crystalline Schiff's bases which may function as tridentate chelate ligands. Their configuration may be represented as follows:



(I) or (II)

[where, R = C_6H_4, $C_6H_3(OH)$ or $C_{10}H_6$]

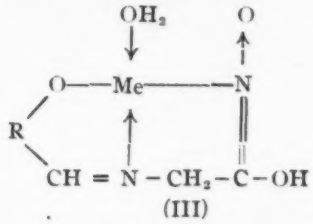
The hydroxamic acids, in general, have been known to exist in two tautomeric forms *a* or *b* (Tieman, *Ber.*, 1889, **22**, 1939; 1891, **24**, 3447, 3453, 4162). Tieman preferred the hydroxamide structure (*a*).



(*a*) or (*b*)

According to Biardo (*Gazzetta*, 1926, **66**, 567) the structure (*a*), however, is incapable of forming metal chelates. But the glycine-hydroxamic acid (Ley, *Ber.*, 1913, **46**, 75; Cunningham, *J. Chem. Soc.*, 1949, 2091; Jones, *J. Amer. Chem. Soc.*, 1917, **39**, 673) has been isolated only in one form. Therefore, the complex ligand (Schiff's base)

may be represented by structure (I) in preference to structure (II), shown above. The metal complexes were usually prepared by the interaction of *o*-hydroxyaldehydes, glycine-hydroxamic acid and the corresponding metal acetates in hot aqueous alcoholic mixture. The metal chelates all show similar physical and chemical properties, and may be represented by the following structure (III).



(III)

[where R = C_6H_4,C_6H_3(OH) or $C_{10}H_6$; Me = Cu^{2+}, Ni^{2+}, Co^{2+} and UO_2^{2+}]

Copper complexes of glycine-hydroxamic acid with different *o*-hydroxyaldehydes are all similar in composition and properties, and show moment values of $1.72-1.82\mu_B$. Hence, the copper chelates have very likely a square planar structure with dsp^2 hybrid bonds. The nickel complexes show paramagnetic moment values of $2.82-2.88\mu_B$, corresponding with the presence of two unpaired electrons as in the simple nickelous ion. This indicates that the bonds in these complexes are of weak covalent type resonating with ionic ones. The nickel complexes are coloured either green or greenish blue. The corresponding cobalt complexes, however, gave three different magnetic moment values. Cobalt-salicylaldehyde-glycinehydroxamate shows a moment value of $4.15\ \mu_B$, corresponding approximately with that for simple cobaltous ion. Hence, the nature of the bonds in this compound is likely to be of the weak covalent type resonating with ionic ones. Cobalt-resorcylaldehyde-glycinehydroxamate and cobalt-β-hydroxynaphthaldehyde-glycinehydroxamate give moment values of 2.58 and $1.57\mu_B$ respectively. The low moment value of the latter compound corresponds practically with the spin moment value of one unpaired electron, and hence, this chelate may be viewed as a penetration complex with dsp^2 planar bonds (Rây, this *Journal*, 1948, **25**, 1). The moment value of 2.58 for the resorcylaldehyde complex seems to suggest that this also belongs to the penetration type with dsp^2 hybrid bonds, but with imperfectly quenched orbital moments of the unpaired electrons. It is rather interesting to note here that ligands of similar composition and structure give rise to complexes of different types, when bound with the cobalt atom. This is possibly associated in some way or other with the difference in the resonating capacity of the complex formed by the different ligands. As resorcylaldehyde and β-hydroxynaphthaldehyde can resonate among a larger number of structures than salicylaldehyde, the complexes involving the first two are likely to possess enhanced stability. The difference may also partly be due to a difference in the steric effect as well as in the basic or acidic character of the ligands. The only uranyl compound that was prepared, *i.e.* uranyl-β-hydroxynaphthaldehyde-glycinehydroxamate, was found to be diamagnetic as usual for hexavalent uranium.

EXPERIMENTAL

General Method of Preparation of the Complexes.—The metal chelate compounds of bivalent copper, nickel, cobalt, and of sexivalent uranium with different *o*-hydroxy-aldehydes and glycine-hydroxamic acid were obtained generally by the interaction of *o*-hydroxyaldehydes (1 mol.), glycine-hydroxamic acid (1 mol.) and the corresponding metal acetates in hot aqueous ethanol mixture. The hydroxyaldehydes and glycine-hydroxamic acid were first refluxed in aqueous alcoholic mixture for 2 to 3 hours on the water-bath, and to the resulting solution of the Schiff's base an aqueous alcoholic solution of the metal acetate (1 mol.) concerned was added, and the mixture was further refluxed on the water-bath for 1 to 2 hours. This was then filtered while hot, and the filtrate on keeping over concentrated sulphuric acid in vacuum yielded the coloured metal chelate. The product obtained was usually purified by recrystallisation from hot ethanol containing a little pyridine.

The same products could also be obtained by the condensation of previously prepared Schiff's base (1 mol.) with metal acetates (1 mol.) in hot aqueous alcoholic medium.

General Properties.—The complex products are generally insoluble or only sparingly soluble in water. These are, however, fairly soluble in many organic solvents like alcohol, acetone, pyridine, dioxan, etc., and dilute alkalies. They are, however, decomposed by dilute mineral acids on warming.

Metal-salicylaldehyde-glycinehydroxamate Complexes

Copper compound: greenish blue crystals. [Found: C, 36.11; N, 9.30; Cu, 20.88; H_2O (by loss at 95°), 9.53. Cu ($C_9H_{10}O_4N_2$), $1.5H_2O$, requires C, 35.92; N, 9.32; Cu, 21.15; H_2O, 9.63 per cent]. [Found (dried at 95°): Cu, 22.62. Calc. Cu: 23.11 per cent].

Nickel compound: light greenish blue crystals. [Found: N, 9.22; Ni, 19.29; H_2O (by loss at 108°), 11.80. Ni ($C_9H_{10}O_4N_2$), $2H_2O$ requires N, 9.18; Ni, 19.25; H_2O, 11.81 per cent].

Cobalt compound: brownish red crystals. [Found: N, 9.42; Co, 19.96; H_2O (by loss at 100°), 9.18. Co ($C_9H_{10}O_4N_2$), $1.5H_2O$ requires N, 9.46; Co, 19.92; H_2O, 9.12 per cent].

Metal-resorcylaldehyde-glycinehydroxamate Complexes

Copper compound: greenish blue shining crystals. [Found: C, 35.80; H, 4.11; N, 9.21; Cu, 21.10; H_2O (by loss at 95°). 5.88. Cu ($C_9H_{10}O_5N_2$), H_2O requires C, 35.11; H, 3.90; N, 9.12; Cu, 20.67; H_2O, 5.85 per cent].

Nickel compound: light orange-yellow crystals. [Found: N, 8.85; Ni, 18.61; H_2O (by loss at 95°), 6.33. Ni ($C_9H_{10}O_5N_2$), $1.5H_2O$ requires N, 8.87; Ni, 18.59; H_2O, 8.55 per cent].

Cobalt compound: orange-brown crystals. [Found: N, 8.75; Co, 18.41; H_2O (by loss at 100°), 11.28. Co ($C_9H_{10}O_5N_2$), $2H_2O$ requires N, 8.73; Co, 18.37; H_2O, 11.22 per cent]. [Found (dried at 100°): Co, 20.73. Calc. Co: 20.70 per cent].

Metal-β-hydroxynaphthaldehyde-glycinehydroxamate Complexes

Copper compound: green crystals, decomposes above 110°. [Found: C, 43.60; H, 4.57; N, 7.84; Cu, 17.71; H_2O (by loss at 105°), 10.08. Cu $(C_{13}H_{12}O_4N_2)$, $2H_2O$ requires C, 43.38; H, 4.45; N, 7.7; Cu, 17.69, H_2O, 10.01 per cent]. [Found (dried at 105°): Cu, 20.01. Calc. Cu: 19.76 per cent].

Nickel compound: reddish brown crystals. [Found: N, 8.30; Ni, 17.41; H_2O (by loss at 100°), 5.31. $Ni(C_{13}H_{12}O_4N_2)$, H_2O requires N, 8.32; Ni, 17.44; H_2O, 5.35 per cent]. [Found (dried at 100°): Ni, 18.46. Calc. Ni: 18.42 per cent].

Cobalt compound: deep chocolate-brown crystals. [Found: N, 8.11; Co, 17.05; H_2O (by loss at 100°), 5.26. Co $(C_{13}H_{12}O_4N_2)$, $1.5H_2O$ requires N, 8.09; Co, 17.05; H_2O, 7.80 per cent].

Uranyl compound: orange-red shining crystals. [Found: C, 29.14; H, 2.53; N, 5.22; U, 44.20. UO_2 $(C_{13}H_{12}O_4N_2)$, $0.5H_2O$ requires C, 28.99; H, 2.41; N, 5.19; U, 44.15 per cent].

Schiff's bases: (1) *Salicylaldehyde-glycinehydroxamic Acid*.—Pure glycine-hydroxamic acid (m.p. 140°) (1 mol.) and salicylaldehyde (1 mol.) in aqueous alcohol were warmed on the water-bath, when orange-yellow shining crystals of the base separated from the solution. These were filtered, washed with cold water and alcohol, and then recrystallised from hot alcohol. The filtrate gave a further crop of crystals on standing.

The substance is slightly soluble in water but fairly so in alcohol, acetone, pyridine, benzene, toluene, dioxan and chloroform. It is decomposed when heated above 115°, and by treatment with dilute mineral acids. The substance dissolves unchanged in dilute alkalies, and reacts with dilute solution of ferric salts, giving a deep violet-red coloration, m.p. 136-38°. [Found: C, 55.28; H, 4.24; N, 14.10. $(OH).C_6H_4CH=NCH_2COHNOH$ requires C, 55.67; H, 5.15; N, 14.43 per cent].

(2) *β-Hydroxynaphthaldehyde-glycinehydroxamic acid* was prepared like the previous compound using β-hydroxynaphthaldehyde in place of salicylaldehyde. It forms yellow shining crystals and resembles the previous compound in properties. [Found: C, 63.96; H, 4.80; N, 11.56. $(OH)C_{10}H_6CH=NCH_2COHNOH$ requires C, 63.93; H, 4.91; N, 11.47 per cent].

The results of magnetic measurements of the different compounds with a field strength of 9.02×10^3 gauss, are recorded in Table I.

TABLE I

Name and colour	$\chi_g \times 10^6$.	$\chi_m \times 10^6$ (Obs.)	$\chi_m \times 10^6$ (Corr.)	Temp.	μ_B effective.
1. Copper-salicylaldehyde-glycine-hydroxamate (green)	3.772	1140	1212	30.2°	1.72
2. Nickel-salicylaldehyde-glycine-hydroxamate (greenish yellow)	10.39	3165	3245	30.2°	2.82
3. Cobalt-salicylaldehyde-glycine-hydroxamate (brownish red)	23.86	7059	7131	30.3°	4.15
4. Copper-resorcylaldehyde-glycinehydroxamate (greenish yellow)	4.233	1302	1394	30°	1.85

TABLE I (contd.)

Name and colour.	$\chi_g \times 10^5$	$\chi_m \times 10^6$ (Obs.).	$\chi_m \times 10^6$ (Corr.).	Temp.	μ_B effective.
5. Nickel-resorcylaldehyde-glycinehydroxamate (orange-yellow)	10.13	3194	3293	30.1°	2.82
6. Cobalt-resorcylaldehyde-glycinehydroxmate (orange-brown)	8.183	2622	2724.8	30.2°	2 58
7. Copper-β-hydroxynaphthaldehyde-glycinehydroxamate (green)	3.505	1261	1348	30.1°	1.82
8. Nickel-β-hydroxynaphthaldehyde-glycinehydroxamate (reddish brown)	9.739	3279	3356	30.2°	2.88
9. Cobalt β-hydroxynaphthaldehyde-glycinehydroxamate (chocolate-brown)	2 679	922.6	1008	30°	1.57
10. Uranyl-β hydroxynaphthaldehyde-glycinehydroxamate (orange-red)	−0.102	−53 96	...	30 5°	Diamagnetic

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GLUCONATE COMPLEX OF TRIVALENT ANTIMONY

By G. Patra and S. Pani

The gluconate complex of trivalent antimony has been investigated from solubility of antimony oxide in partially neutralised gluconic acid solutions. The complex (I) is formed. The equilibrium constant K_1 of the reaction in which the above complex is formed from antimonyl ion and gluconate ion is not strictly constant, but increases with increasing percentage of neutralisation of gluconic acid (*i e.* with increasing p_H). This variation is due to the dissociation of the complex (I) like a monobasic acid and the dissociation constant has been determined.

The variation of K_1 with p_H could be explained if it is assumed that the co-ordination positions occupied by gluconate ligand increase from three to four at higher p_H. It has been shown that such increase is less probable.

A number of antimony chelates have been investigated by S. Pani and his co-workers (this *Journal*, 1955, **32**, 197, 161, 217). The co-ordination number of antimony in all cases is four. The results of investigation with a more complex (gluconate) ligand is discussed here.

Experimental

The chemicals used were of Analar quality, and freshly prepared antimony oxide was used. The solubility of antimony oxide in partially neutralised gluconic acid solutions of known concentration was determined, and p_H was measured (after Mohanty and Pani, *ibid.*, 1954, **31**, 593). Three sets of experiments were done and in each set gluconic acid neutralising to the same extent was used. The results are shown in Table I.

Table I

Neutralisation of gluconic acid.	Total gluconate.	p_H.	Total antimony.	$[SbC] \times 10^2$.	$[Gl^-] \times 10^2$.	$K_1 \times 10^{-6}$.	$K_2 \times 10^{-2}$.
	0.50	3.10	0.0630	6.294	11.26	0.915	7.26
	0.40	3.08	0.05615	5.609	8.555	1.02	8.52
25%	0.30	3.07	0.04560	4.554	6.220	1.12	9.51
	0.20	3.07	0.03644	3.638	4.000	1.19	11.8
	0.10	3.15	0.1791	1.785	2.301	1.42	10.1
	0.05	3.25	0.00790	0.7842	1.386	1.31	7.34
	0.50	3.74	0.07040	7.034	25.87	1.94	3.53
	0.40	3.74	0.05990	5.984	20.48	2.08	3.79
50%	0.30	3.76	0.04755	4.749	15.48	2.29	3.98
	0.20	3.81	0.04508	4.502	9.917	3.81	5.82
	0.10	3.84	0.01976	1.970	5.266	2.71	3.92
	0.05	3.85	0.01019	1.013	2.635	3.53	4.99
	0.50	4.42	0.05436	5.430	39.16	4.74	1.80
	0.40	4.46	0.05002	4.996	31.09	6.02	2.09
75%	0.30	4.48	0.03800	3.794	23.40	5.05	1.67
	0.20	4.56	0.03026	3.010	15.48	9.19	2.53
	0.10	4.64	0.01730	1.724	7.67	13.40	2.92
	0.05	4.60	0.008028	0.797	3.852	10.70	2.69

The concentrations are expressed in g. moles per litre.

Discussion

Besides the carboxyl group, there are five hydroxyl groups in the gluconate ligand. It is, however, not possible to say how many co-ordination positions would be occupied by the gluconate ligand. It is assumed that the co-ordination number of antimony would be four, as observed in other complexes. The positions of the carboxyl group and the two hydroxyl groups adjacent to it are similar to those of the bitartrate ligand which reacts with antimony in the formation of antimonyl tartrate ion (Tartrate complex of antimony, Samantara, Rao and Pani, *loc.cit.*, p. 197 ; Reihlen and Hezel, *Annalen*, 1931, **487**, 213). It is therefore probable that gluconate ion may occupy more than two co-ordination positions, and in such a case the complex would contain one gluconate ligand per antimony atom.

It is assumed that antimonyl ion present in the aqueous solution of antimony oxide reacts with n gluconate ligands and the complex SbC is formed. The change of the complex (not shown) would depend on n and the co-ordination positions occupied by the gluconate ligand. Hydrogen ions would be liberated if the hydroxyl group would react, and the number of hydrogen ions liberated (m) would again depend on n and the co-ordination positions occupied by gluconate ligand. The reaction may be represented by equation (1) and the equilibrium constant of the reaction by equation (2), where [SbC], [H^+], [SbO^+] and [Gl^-] represent the molar concentrations of the complex, hydrogen ion, antimonyl ion and gluconate ion respectively.

$$SbO^+ + n\ Gl^- \rightleftharpoons SbC + m\ H^+ + H_2O \qquad \ldots \qquad \ldots \quad (1)$$

$$\frac{[SbC] \times [H^+]^m}{[SbO^+] \times [Gl^-]^n} = K \qquad \ldots \qquad \ldots \quad (2)$$

Taking the concentration of hydrogen ion to be constant in each set of experiments and substituting [SbO^+] by $7.7 \times 10^{-4} \times [H^+]$ (Gayer and Garrett, *J. Amer. Chem. Soc.*, 1952, **74** 2353) it can be shown that equations (3) and (4) hold for each set of experiments.

$$\frac{[SbC]}{[Gl^-]^n} = K_1 \qquad \ldots \qquad \ldots \qquad \ldots \quad (3)$$

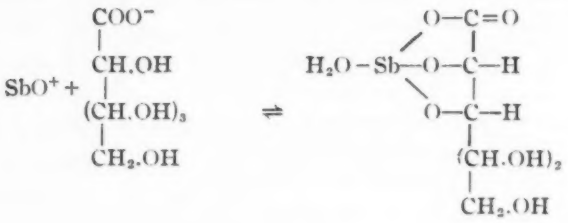
$$\log [SbC] = \log K_1 + n \log [Gl^-] \qquad \ldots \qquad \ldots \quad (4)$$

The value of n would be equal to slope of the line obtained by plotting log [SbC] against log [Gl^-]. [SbC] is obtained by subtracting the solubility of antimony oxide in water (5.8×10^{-5} g. atoms of Sb per 1000 g. of water ; Gayer *et al.*, *loc. cit.*) from the total antimony in the solution. Unreacted or free gluconate is obtained by subtracting the gluconate present in the complex, from total gluconate [Gl^-] by assuming n to be equal to 1 or 2. Thus two sets of values of unreacted gluconate are obtained. Two sets of values of [Gl^-] are calculated by equation (5) where k is the dissociation constant of gluconic acid $= 2.75 \times 10^{-4}$ (Cannan and Kibrick, *ibid.*, 1938, **60**, 2314).

$$[Gl] - n\ [SbC] = \text{unreacted gluconate} = [Gl^-] \times \left\{ 1 + \frac{[H^+]}{k} \right\} \qquad \ldots \quad (5)$$

Log [SbC] is plotted against log [Gl^-] and it is found that the slope of the line (in the case where [Gl^-] has been calculated by assuming n to be 1) is very nearly 1. Gluconate ligand most probably occupies more than two (three or four) co-ordination positions since there is one gluconate ligand per antimony atom in the complex.

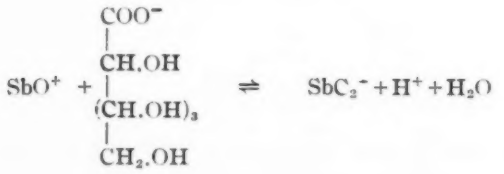
If gluconate ligand occupies three co-ordination positions, it is probable that the complex would be similar to antimonyl tartrate ion, and the reaction may be represented by equation (I) and the equilibrium constant by (I-1).



... (I)

$$\frac{[SbC_1]}{7.7\times10^{-4}\times[H^+]\times[Gl^-]} = K_I \qquad \ldots \text{(I-1)}$$

The above complex, though a neutral molecule, is expected to be soluble in water since there are a large number of polar groups in the molecule. If, however, gluconate ligand is tetradentate, it is not possible to say which of the three free hydroxyl groups, shown in the above complex in equation (I), would react to occupy the fourth co-ordination position, since the two five-membered rings, shown in the above structure, would not be present in one plane. The complex (if formed) may be represented by SbC_2^- (there would be one unit of negative charge), and the reaction by equation (II) and the equilibrium constant by equation (II-1).



... (II)

$$\frac{[SbC_2^-]}{7.7\times10^{-4}\times[Gl^-]} = K_{II} \qquad \ldots \qquad \ldots \text{(II-1)}$$

Assuming that either reaction (I) or reaction (II) takes place throughout the range of investigation, K_I or K_{II} is calculated. [SbC_1] or [SbC_2^-] is taken as equal to [SbC], discussed previously. [Gl^-] is calculated by equation (5), substituting n by 1.

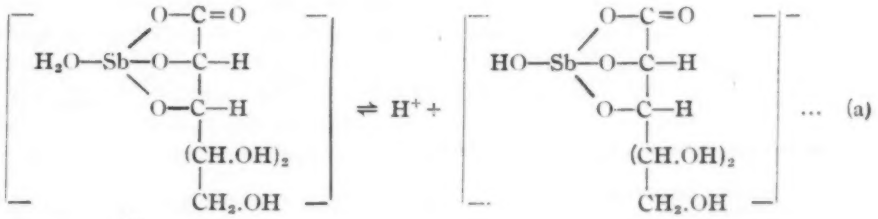
The calculated values of K_I and K_{II} are shown in Table I. None of these are strictly constant ; K_I increases whereas K_{II} decreases with increasing p_H.

The results indicate that two different species of complex exist. K_I can be taken as constant at lower p_H range. It can therefore be assumed that the complex SbC_1 exists in pure gluconic acid solution, the concentration of the other species being very small. K_I can also be taken as constant at lower p_H range. The existence of the complex SbC_2^- therefore appears to be probable at low p_H range. The system would, however, be continuous and since K_{II} is equal to $K_I \times [H^+]$, complex SbC_1 is very likely to be converted into the other complex by the liberation of a hydrogen ion. This is possible if the co-ordination positions (three) occupied by gluconate ligand in the complex SbC_1 are increased by one as the p_H is increased. The reaction (if possible) is represented by equation (III) :

$$(I) \rightleftharpoons SbC_2^- + H^+ + H_2O \quad \ldots \quad \ldots \quad (III)$$

It is, however, less probable due to the following reasons. The alcoholic group does not ionise to produce hydrogen ion with increasing p_H ; hence the above reaction (III) is not likely to occur to any appreciable extent by change in the concentration of hydrogen ion. The gluconate ligand would occupy four co-ordination positions only if one of the three hydroxyl groups present in the complex SbC_1 can come near the antimony atom so that a bond between the antimony and the oxygen atom can be formed. This would depend on steric effect, but not on p_H. The tetrahedral distribution of valency bonds of carbon atom is favourable for the formation of five- or six-membered rings. If the carbon atoms are favourably oriented, the hydroxyl group of the fifth or sixth carbon atom (carbon atom of the carboxyl group is taken as the first carbon atom) can come near the oxygen atom of the third carbon atom which (oxygen atom) is already bonded to the antimony atom. In both the cases there would be repulsion.

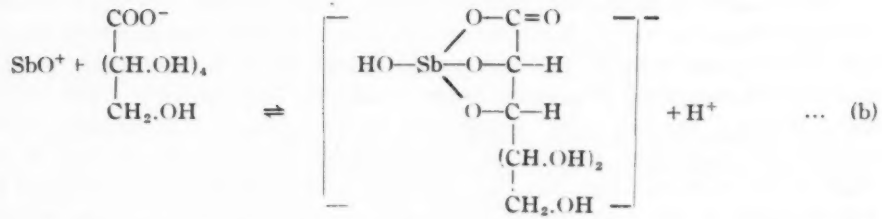
Probably complex SbC_2^-, in which gluconate ligand occupies four co-ordination position, is not formed. The other possibility is the ionisation of the complex SbC_1 like a monobasic acid into hydrogen ion and another complex, say, SbC_1^-, as shown in equation (a). There is no structural change.



(I) ... (a)

$$\frac{[SbC_1^-] \times [H^+]}{[SbC_1]} = K_a \quad \ldots \quad (a\text{-}1)$$

The equilibrium constant of the reaction, by which the complex SbC_1^- is formed from antimonyl ion and gluconate ion would be equal to K_{II} and is evident from the equation (b) shown below.



The reaction (a) would be favoured by increasing p_H. It is therefore most probable that at lower p_H the reaction is predominantly (I) and most of the antimony in solution is present as complex SbC_1. As the p_H is increased, the reaction (a) proceeds in the forward direction and the concentration of SbC_1^- progressively increases.

The actual value of K_1 is obtained by extrapolating curve, obtained by plotting the average value of K_1 in each set of experiments against the percentage of neutralisation, to zero neutralisation of gluconic acid. The value obtained is 8.00×10^{-5}. Utilising this value of K_1, the concentrations of SbC_1 is calculated by equation (I-1) for all the three sets of experiments. The concentration of SbC_1^- is obtained by subtracting $[SbC_1]$ and the solubility of antimony oxide in water from the total antimony in the solution. The equilibrium constants of the reaction (a), given by the equation (a-1), are calculated and shown in Table II. Except in very few cases, the value of K_a is fairly constant and the mean value is 3.07×10^{-4}.

TABLE II

p_H.	$[SbC_1] \times 10^2$.	$[SbC_1^-] \times 10^2$	$K_a \times 10^4$.	p_H.	$[SbC_1] \times 10^2$.	$[SbC_1^-] \times 10^2$.	$K_a \times 10^4$.
3.10	5.507	0.787	1.14	3.81	0.9462	3.556	5.82
3.08	4.383	1.226	2.33	3.84	0.4691	1.501	4.63
3.07	3.262	1.292	3.37	3.85	0.2293	0.784	6.08
3.07	2.097	1.541	6.25	4.42	0.9173	4.513	1.87
3.15	1.003	0.782	5.52	4.46	0.6640	4.332	2.27
3.25	0.480	0.3042	4.49	4.48	0.4774	3.317	2.30
3.74	2.900	4.134	2.59	4.56	0.2620	2.748	2.89
3.74	2.296	3.688	2.92	4.64	0.1034	1.621	3.43
3.76	1.658	3.091	3.24	4.60	0.0596	0.7374	3.11
						Mean	3.07

The concentrations are expressed in g. moles per litre.

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STUDIES ON CORCHORIN. PART I

By Md. Moslemuddin and Mofizud-din Ahmed

Corchorin yields glucose and corchogenin on acid hydrolysis. Corchogenin forms acetate, dibromide, oxime, semicarbazone and dichloro derivatives. These show the presence of one hydroxyl group, a double bond and an aldehydic group in the molecule of the genin.

Although Tsuno (*Monatsh. Tierheil.*, 1895, **6**, 445) reported the occurrence of a bitter principle, 'corchorin', in jute seeds, it was Sen (this *Journal*, 1930, **7**, 83), who isolated it as rhombic prisms, m.p. 174-75°, having intense bitter taste and properties of the digitalis groups of saponins (Sen and Das, *Indian J. Physiol.*, 1948, **2**, 1). On acid hydrolysis of corchorin, Sen (this *Journal*, 1930, **7**, 903) obtained one mole of glucose and one mole of a crystalline aglucone, m.p. 112-14°, which he named corchogenin and gave the formula $C_{16}H_{26}O_3$. Further, he prepared from the corchogenin a dibromide, m.p. 130-32°, a monochloro derivative with phosphorus pentachloride and an impure phenylhydrazone, m.p. 165-70° but failed to obtain an oxime as well as a semicarbazone. Soliman and Saleh (*J. Chem. Soc.*, 1950, 2198) isolated corchorin to which they assigned the formula $C_{23}H_{32}O_6$, 0.5 H_2O, m.p. 175-77° (decomp.). They prepared from corchorin a crystalline acetyl derivative, m.p. 243-44°, an oxime, m.p. 265-70° (decomp.) and a phenylhydrazone, m. p. 240-43°. They reported absence of sugar moiety in the corchorin and showed it to be identical with strophanthidin from a comparison of the formula, melting points and properties of corchorin and its derivatives. Chaudhury and Dutt (this *Journal*, 1951, **28**, 167) reported isolation of pure corchorin, m.p. 177-78°. It has been reported earlier (Alam *et al.*, *Cur. Sci.*, 1954, **23**, 332) that corchorin, isolated from various samples of *C. capsularis* and *C. olitorius*, yielded a mole of glucose and corchogenin, $C_{17}H_{22}O_3$, when hydrolysed with sulphuric acid.

For this investigation (and also for the previous one) corchorin was obtained along with another bitter, *corchsularin* (Khalique and Ahmed, *J. Org. Chem.*, 1954, **19**, 1523), by a simplified method from different varieties of Jute seeds. Corchorin, thus obtained, had m.p. 177-78° (decomp.) and no water of crystallisation. The formula came out to be $C_{23}H_{32}O_6$ from analytical data. Its hydrolysis to glucose and corchogenin took place in accordance with the equation :

$$C_{23}H_{32}O_6 + H_2O = C_6H_{12}O_6 + C_{17}H_{22}O_3.$$

Corchogenin, thus obtained, formed a monoacetate, m.p. 123-24°, a monochloro derivative instantaneously and a dichloro derivative on prolonged standing with concentrated hydrochloric acid. This is indicative of the presence of one acetylable and another tertiary hydroxyl group (cf. Jacobs and Gustus, *J. Biol. Chem.*, 1929, **82**, 408) in the molecule of the genin. Corchogenin reduced Tollen's reagent and gave an oxime, m.p. 79-80° and semicarbazone, m.p. 230-32°, showing the presence of an aldehydic group. The formation of a dibromide showed the presence of a double bond.

While Soliman and Saleh (*loc. cit.*) observed loss of bitterness on crystallisations (charcoal) from dilute ethanol or methanol, corchorin obtained by the authors retained its bitterness after alternate process of charcoal treatment and repeated crystallisations. Corchorin was bitter in dilutions over 1 in 100,000. Pure corchorin failed to give red coloration with green fluorescence on addition of H_2SO_4 (conc.) although impure variety developed such coloration. Corchogenin also failed to respond to sodium nitroprusside test (*J. Biol. Chem.*, 1926, **67**, 336).

In view of the above observation, it seems that Soliman and Saleh (*loc. cit.*) obtained a bitter substance other than corchorin. It is of interest to note that recently Frerejacque and Durgeat (*Compt. rend.*, 1954, **238**, 507) reported isolation from jute seeds of a bitter, *corchorside A*, which yielded strophanthidin and a sugar, yet to be identified on hydrolysis.

Experimental

Isolation of Corchorin.—Finely powdered jute seeds (in batches of 500 g.) were extracted with rectified spirit in a Soxhlet apparatus. Alcohol was distilled off the extract under reduced pressure and the residue was digested with water (about 1 litre) and filtered while hot. The reddish brown filtrate was treated with a saturated solution of lead acetate, and filtered. Into the clear filtrate was passed excess of hydrogen sulphide to remove the excess of lead ions and then carbon dioxide to remove the excess of hydrogen sulphide in turn. The brownish solution, thus obtained, yielded on concentration needle- and prism-shaped crystals, m.p. 160-64° (decomp.), which were collected, dissolved in rectified spirit (250 c.c.) and refluxed with activated charcoal (75 g., Technical quality, B. D. H.) for 30 minutes, cooled and filtered. A fresh quantity of activated charcoal (5 g.) was again added to the filtrate, refluxed, cooled and again filtered. This process was continued till activated charcoal failed to adsorb. The filtrate, thus obtained, furnished on concentration colorless rhombic prisms which melted at 177-78° (decomp.) after several crystallisations from dilute ethanol. It had $[\alpha]_D^{25} = +32°.86$ (in methanol). [Found: C, 64.36; H, 7.38; M.W. (cryoscopic, acetic acid), 428.6. $C_{23}H_{32}O_8$ requires C, 63.30; H, 7.34 per cent. M.W., 434]. Corchorin is soluble in methanol, ethanol, acetone, pyridine and acetic acid. In Table I is recorded the amount of corchorin obtained from *C. olitorius* and various species of *C. capsularis*.

Table I*

%Corchorin in various jute seeds.

Species and varieties of seeds.	% Yield.
C. capsularis, Linn.	
Var. D-154	0.90
Var. C 39-219	0.85
Var. C 41-13	0.83
Var. C 42-Nj 412	0.84
C. olitorius, Linn.	0.92

* Determined by Dr. A. Khalique. Seeds were supplied by the Director of Agriculture, E. Bengal, which the authors are indebted to him.

Treatment with activated charcoal for purification of corchorin by the method of Khalique and Ahmed (*loc. cit.*) afforded corchsularin, m.p. 157-58° (decomp.).

Water of crystallisation.—Corchorin crystals were heated over calcium chloride at 80° under vacuum for a period of 12 hours but no loss of water was obtained. The same sample lost half a mole of water when heated at 110° under vacuum for 12 hours. The dehydrated sample softened at 154-55° and melted at 164° (decomp.). This on crystallisation from dilute ethanol softened at 147° and melted at 213-15° (decomp.).

Hydrolysis of Corchorin.—Corchorin was hydrolysed to glucose and *corchogenin* by the method of Alam *et al.* (*loc. cit.*). Corchorin melted at 114-16° when crystallised from ether-ethanol. [Found: C, 73.45; H, 8.01; M.W. (Rast), 273.8. Calc. for $C_{17}H_{22}O_3$: C, 74.45; H, 8.03 per cent. M.W., 274].

Acetylation of Corchogenin.—To a solution of corchogenin (0.09 g.) in pure pyridine (10 c.c.) was added acetic anhydride (20 c.c.) gradually. The mixture was refluxed for 4 hours on a steam-bath, cooled and poured into ice water (100 c.c.). Fine crystals of *corchogenin acetate* appeared when left overnight in open space. After several crystallisations from dilute ethanol and drying over calcium chloride, the crystals melted at 123-24°. (Found: acetyl, 13.55. $C_{19}H_{24}O_4$ requires for *one* acetyl, 13.60 per cent).

Oxime.—To an aqueous solution of hydroxylamine hydrochloride (0.5 g. in 2 c.c. water) were added 10% sodium hydroxide solution (2 c.c.), corchogenin (0.2 g.) and sufficient dilute ethanol to dissolve the genin. The mixture was warmed for 10 minutes in a water-bath, cooled and then diluted to double of its volume. Slow concentration afforded the *oxime* as prismatic crystals, which melted at 79-80° after drying over calcium chloride. (Found: N, 4.34. $C_{17}H_{23}O_3N$ requires N, 4.77 per cent).

Semicarbazone.—Corchorin (0.1 g.) was dissolved in ethanol and to it was added water until the solution was faintly turbid, which was then removed by addition of a little ethanol. To this were added semicarbazide hydrochloride (1.0 g.) and crystalline sodium acetate (1.5 g.), and the mixture was shaken vigorously, heated in boling water and cooled. Upon standing in open space for several days, orange-coloured prismatic crystals of the carbazone, m.p. 230-32°, appeared. It was hygroscopic. (Found: N, 11.88. $C_{18}H_{25}O_3N_3$ requires N, 12.68 per cent).

Corchogenin Dibromide.—To corchorin (0.85 g.), dissolved in chloroform (20 c.c.), was added a solution of bromine in the same solvent until the colour of bromine persisted. The mixture was left for 12 hours at room temperature and then refluxed for an additional hour. The excess of bromine and chloroform were removed by distillation and water (30 c.c.) was added to it when a yellow amorphous substance precipitated. The precipitate of *corchogenin dibromide* was collected, washed with sulphurous acid and dried. Crystallisation from a mixture of alcohol and ligroin furnished yellow crystals, which sintered at 109° and melted at 120-21° (decomp.). (Found: Br, 36.41. $C_{17}H_{22}O_3Br_2$ requires Br, 36.86 per cent).

Action of Hydrochloric Acid.—HCl (conc., 10 c.c.) was cooled in an ice-bath and to it was added corchorin (0.5 g.) with stirring when *chlorocorchogenin* precipitated in thick mass instantaneously. The precipitate was collected, washed free of

hydrochloric acid and finally crystallised from absolute alcohol. It had m.p. 75-76°. (Found: Cl, 11.71. $C_{17}H_{21}O_2Cl$ requires Cl, 12.13 per cent).

The solution after separation of chlorocorchogenin was left in the ice-bath for 2 hours. On addition of ice-water (30 c.c.) to it, a voluminous precipitate of *dichloro-corchogenin* separated out. This was collected, washed free of hydrochloric acid and dried over calcium chloride in vacuo. It melted at 121-22°. (Found: Cl, 22.33. $C_{17}H_{20}OCl_2$ requires Cl, 22.83 per cent). Its alcoholic solution deposited silver chloride when boiled with silver nitrate.

Action of Nitric Acid.—Corchorin (1.2 g.) was added to nitric acid (conc., 40 c.c.) when it dissolved to a brown solution, which was refluxed for 6 hours and then concentrated to one fourth of its original volume. Addition of water formed voluminous precipitate, m.p. 87-90°. This was soluble in alcohol, acetone, ether; moderately soluble in chloroform and insoluble in water, benzene and petroleum ether. As it was not possible to crystallise it, further work was not attempted.

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INNER-METALLIC COMPLEX SALTS OF HYDROXYALDIMINO ACIDS WITH POLYCYCLIC RINGS. PART I

By Ajit Kumar Mukherjee and Priyadaranjan Rây

In continuation of the previous work, a number of complex compounds of bivalent copper, nickel, cobalt and manganese, with resorcylaldehyde or β-hydroxy-α-naphthaldehyde and amino-acids like glycine, alanine or anthranilic acid have been prepared and their properties studied.

The configurations of these complexes like the corresponding inner-metallic complex salts of salicylaldimino acids, cannot always be represented by unique and unambiguous structural formulae. Preference has been given to the most probable of all the possible structures on the basis of their properties like solubility, colour, magnetic susceptibility, etc. As with salicylaldehyde, the hydroxyaldehydes in these complexes are believed to undergo condensation with amino-acids, giving rise to 'hydroxylaldimine acids' which can function under suitable conditions as a tridentate or bidentate ligand.

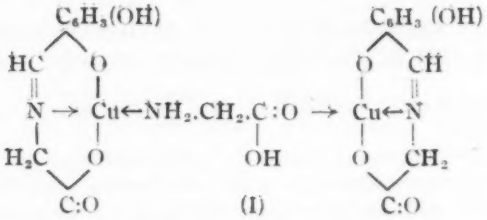
Pfeiffer and co-workers (*J. prakt. Chem.*, 1931, **129**, 163; 1936, **145**, 243; 1940, **151**, 145; 1942, **155**, 77; **159**, 313; *Annalen*, 1933, **503**, 84; *Z. angew. Chem.*, 1940, **53**, 93; *Ber.*, 1944, **77A**, 59) studied the preparation, properties and constitution of a number of metal chelate complexes of oxyaldimines and oxyketimines with spiral-like or polycyclic rings. Similar metal chelate complexes of salicylaldimino acids with polycyclic rings were prepared and studied by us (Rây and Mukherjee, this *Journal*, 1950, **27**, 707; 1955, **32**, 493). The configuration of those complexes could not always be represented by unique and unambiguous structural formulae. The salicylaldehyde molecule in the complexes is believed to undergo condensation with different amino-acids giving rise to what was termed as 'aldimine acids' which could function as both tridentate and bidentate ligands under suitable conditions. In continuation thereof we have now succeeded in preparing and studying a number of similar chelate complexes of copper, nickel, cobalt and manganese with resorcylaldehyde or β-hydroxy-α-naphthaldehyde and different amino-acids like glycine, alanineor anthranilic acid.

The complexes were usually obtained by the interaction of the acetate of the metals, amino-acid and the corresponding hydroxyaldehyde in aqueous alcoholic medium. The Schiff's bases formed by the interaction of the hydroxyaldehydes and amino-acids usually function as tridentate ligand. But in some cases these were found to behave like the salicylaldimino acids (*loc. cit.*) as bifunctional units with their carboxylic acid group remaining free. The composition and nature of these complexes also have been found to vary with the nature of the central metal atom as also with the nature of the ligand. The magnetic susceptibilities of all these compounds were measured with the help of Gouy's balance, and the structure and the bond types involved in their formation have been deduced therefrom.

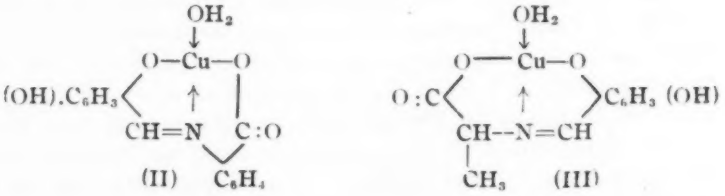
Copper Compounds

Copper-resorcylaldehyde-glycine complex was found to be similar to the corresponding salicylaldehyde complex in composition (Rây and Mukherjee, *loc. cit.*). Its

magnetic moment value of 1.72 μ_B and its high solubility in water and alkalies support the configuration (I).



Copper-resorcylaldehyde-alanine and copper-resorcylaldehyde-anthranilate behave similarly in their properties. In these complexes the 'hydroxyaldimine acid' ligand behaves as a tridentate unit. The composition of the copper-resorcylaldehyde-anthranilate is also similar to that of the corresponding salicylaldehyde complex (this *Journal*, 1950, **27**, 709), but copper-resorcylaldehyde-alanine differs in composition from the corresponding salicylaldehyde compound (Rây and Mukherjee, *loc.cit.*). These two compounds may therefore be represented as (II) and (III) respectively.



The properties of these compounds and their comparatively low magnetic values (1.81 and 1.75 μ_B respectively) support the above structures. It can therefore be concluded that planar dsp^2 hybrid bonds are involved in their formation (Rây and Sen, this *Journal*, 1948, **25**, 473).

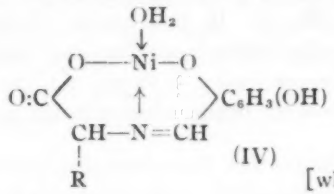
The corresponding copper compounds of β-hydroxy-α-naphthaldehyde and amino-acids possess similar composition and properties. In these chelate compounds the hydroxyaldimine acids function as a tridentate ligand as in resorcylaldehyde-alanine and-anthranilate complexes. The magnetic moment values of the glycine and alanine complexes (1.79 and 1.81 μ_B respectively) suggest that they may be regarded as penetration complexes with planar dsp^2 bonds, whereas the moment value of 2.05 μ_B for the anthranilic acid complex indicates its ionic character or a structure with sp^2d planar bonds (Rây and Sen, *loc. cit.*).

Nickel Compounds

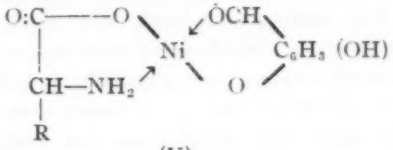
All the nickel compounds that have been prepared and examined show paramagnetic moments of about 3 μ_B corresponding to the presence of two unpaired electrons, indicating that the bonds in these complexes are of the weak covalent type, resonating with ionic ones. In this respect they behave like the corresponding salicylaldimino

acid complexes (Rây and Mukherjee, *loc. cit.*). These compounds are either coloured green or greenish brown.

Nickel-resorcylaldehyde-glycine and nickel-resorcylaldehyde-alanine are insoluble in water. The configuration of these complexes may be represented by formula (IV) in preference to (V), which may be viewed as a molecular compound of nickel-resorcylaldehyde with nickel-glycine or nickel-alanine, as the case may be.



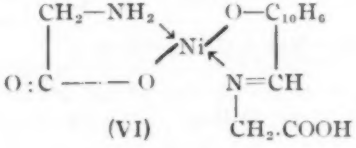
(IV)



(V)

[where R = H or CH_3]

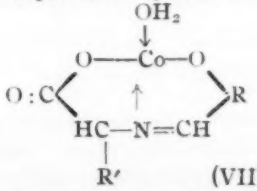
The nickel-β-hydroxynaphthaldehyde-alanine complex shows properties and composition similar to those of the corresponding resorcylaldehyde complexes. It may therefore be represented by a similar configuration (cf. IV). But the nickel-β-hydroxynaphthaldehyde-glycine complex, however, behaves in a different manner and resembles the nickel, salicylaldehyde-alanine complex (Rây and Mukherjee, *loc. cit.*). This glycine compound is soluble in water and in organic solvents. It can be represented by structure (VI) similar to that of the corresponding salicylaldehyde-alanine complex:



(VI)

Cobalt Compounds

Cobalt-resorcylaldehyde-alanine complex resembles in its solubility and structure nickel-salicylaldehyde-alanine and the cobalt-salicylaldehyde-glycine (this *Journal*, 1950, **27**, 711) as also complex (VI). The substance is soluble in water and gives a moment value of 2.17 μ_B, corresponding practically with the spin moment of one unpaired electron, slike the cobalt-alicylaldehyde-glycine compound. This suggets the formation of planar square dsp^2 bonds, characteristic of the penetration complexes of the inner-metallic type. Cobalt-resorcylaldehyde-glycine, cobalt-β-hydroxynaphthaldehyde-glycine and -alanine complexes, on the other hand, behave differently. The 'hydroxyaldimine acid' in these com-plexes may be regarded to function as a tridentate ligand. These complexes are there-fore best represented by structure (VII).



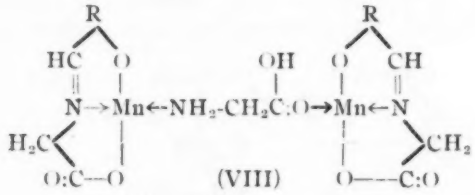
(VII)

[where, R = C_6H_3 (OH) or $C_{10}H_6$; and R′ = H or CH_3]

Cobalt-resorcylaldehyde-glycine and cobalt-β-hydroxynaphthaldehyde-alanine show moment values of 4.49 and 4.51 μ_B respectively, corresponding approximately with that for cobaltous ion. Hence, the bonds in these complexes are possibly of the weak covalent type, resonating with ionic ones. The cobalt-β-hydroxynaphthaldehyde-glycine, on the other hand, shows a moment value of 1.58 μ_B, corresponding practically with the spin moment of one unpaired electron. It may therefore be viewed as a penetration complex with dsp^2 square planar bonds (Rây, *ibid.*, 1948, **25**, 3). In this respect it resembles the cobalt-salicylaldehyde-anthranilate, cobalt-salicylaldehyde-alanine and cobalt-salicylaldehyde-glycine complexes (Rây and Mukherjee, *loc.cit.*). It shows that the nature of the aldehyde leads to a change in the nature of the bonds involved in the formation of the cobalt 'hydroxyaldimine acid' complexes.

Manganese Compounds

The manganese-resorcylaldehyde- and -β-hydroxynaphthaldehyde-glycine complexes resemble in their composition and behaviour the corresponding salicylaldehyde-glycine and -alanine complexes, as well as the copper-salicylaldehyde and-resorcylaldehyde-glycine complexes. The compounds are therefore represented by configuration (VIII).



(VIII)

[where R = $C_6H_3(OH)$ or $C_{10}H_6$]

The corresponding hydroxyaldehyde-alanine complexes of manganese, however, differ from the above type and behave like the corresponding copper, nickel and cobalt complexes. The hydroxyaldimine acids function here as a tridentate chelating unit. These are therefore represented like the copper-resorcylaldehyde-alanine complex (III).

All these manganese compounds give moment values of near about 6 μ_B, which corresponds with that for the simple manganous ion. Therefore, the bonds in these complexes are weakly covalent, resonating with the ionic type.

EXPERIMENTAL

General Method of Preparation of the Metal Chelate Complexes with Resorcylaldimino Acids

The metallic chelate compounds of bivalent copper, nickel, cobalt and manganese ions with resorcylaldehyde and amino-acids were usually prepared by the interaction of resorcylaldehyde (2 mols.), amino-acid (2 mols.) and the corresponding metal acetate (1 mol.) in hot aqueous alcoholic mixture.

These compounds could also be obtained in the pure state by the condensation in equimolecular quantities of different metal-resorcylaldehyde complexes with the corresponding amino-acids. The products obtained were usually purified by recrystallisation from hot aqueous alcohol, containing a little pyridine.

1. *Copper-resorcylaldehyde-glycine* forms shining greenish blue needle-shaped crystals which are soluble in water, pyridine and alcohol, and practically insoluble in acetone and chloroform. These are decomposed by dilute mineral acids on warming, but unaffected by dilute alkalies. [Found : N, 7.16 ; Cu, 21.71 ; resorcylaldehyde, 46.98. $Cu_2(C_9H_7O_4N)_2$. $NH_2.CH_2.COOH$ requires N, 7.14 ; Cu, 21.63 ; resorcylaldehyde, 46.88 per cent].

Copper was estimated iodimetrically after decomposition of the substance with H_2SO_4 (conc.) and a little HNO_3 (conc.). Nitrogen was estimated as usual by microcombustion (Dumas' method). Resorcylaldehyde was estimated as copper-resorcylaldoxime as in the case of salicylaldehyde in salicylaldimino complexes (Rây and Mukherjee, *loc. cit.*, 1950).

2. *Copper-resorcylaldehyde-alanine* forms shining green crystals which are soluble in alcohol, pyridine, acetone, benzene and dioxan, but only sparingly soluble in hot water. [Found : N, 4.35 ; Cu, 19.62 ; resorcylaldehyde, 42.88 ; H_2O (by loss at 105°), 11.12. Cu $(C_{10}H_{11}O_5N)$, $2H_2O$ requires N, 4.31 ; Cu, 19.60 ; resorcylaldehyde, 42.50 ; H_2O, 11.07 per cent].

3. *Copper-resorcylaldehyde-anthranilate* forms shining green crystals. These are only sparingly soluble in water, but readily soluble in alcohol, pyridine, acetone and benzene. [Found : Cu, 18.93 ; C, 50.16 ; H, 3.36 ; N, 4.18. Cu $(C_{14}H_{11}O_5N)$ requires Cu, 18.90 ; C, 49.91 ; H, 3.27 ; N, 4.16 ; per cent].

4. *Nickel-resorcylaldehyde-glycine.*—The light green crystals of the substance are sparingly soluble in water, but fairly soluble in dilute pyridine and acetone. [Found : Ni, 19.22 ; N, 4.60 ; C, 35.36 ; H_2O (by loss at 105°), 11.69. $Ni(C_9H_9O_5N)$, $2\ H_2O$ requires Ni, 19.19 ; N, 4.58 ; C, 35.53 ; H_2O, 11.58 per cent]. [Found (dried at 105°) : Ni, 21.76. Calc. Ni : 21.74 per cent].

Nickel was estimated as nickel-dimethylglyoxime after decomposition of the substance with H_2SO_4 (conc.) and a little HNO_3 (conc.).

5. *Nickel-resorcylaldehyde-alanine* forms chocolate brown crystals and resembles the previous compound in properties. [Found : Ni, 20.08 ; N, 4.80 ; C, 41.32 ; H, 4.50. Ni $(C_{10}H_{11}O_5N)$, $0.5\ H_2O$ requires Ni, 20.08 ; N, 4 78 ; C, 41.01 ; H, 4.10 per cent].

6. *Cobalt-resorcylaldehyde-glycine* forms orange-red crystals and is sparingly soluble in water, but fairly so in hot alcohol, acetone and pyridine. [Found : Co, 21.13 ; C, 39.23 ; H, 3.71 ; N, 5.04. Co $(C_9H_9O_5N)$, $0.5\ H_2O$ requires Co, 21.13 ; C, 38.73; H, 3.58 ; N, 5.2 per cent].

Cobalt was estimated as cobalt sulphate after decomposition with H_2SO_4 (conc.) and a little HNO_3 (conc.).

7. *Cobalt-resorcylaldehyde-alanine* forms reddish brown crystals, soluble in water and pyridine, but sparingly soluble in alcohol, acetone and benzene. It reacts slightly acidic to litmus. [Found : C, 44.02 ; Co 16.64 ; N, 8.08. Co ($C_{13}H_{16}O_6N_2$) requires C, 43.95 ; Co, 16.61. N, 7.88 per cent].

8. *Manganese-resorcylaldehyde-glycine'* forms brown crystals, sparingly soluble in cold water and alcohol, but fairly soluble in pyridine and dioxan. Its aqueous solution is slightly acidic to litmus. [Found : Mn, 19.25 ; C, 43.11 ; H, 3.62 ; N, 7.36. $Mn_2(C_9H_7O_4N)_2.NH_2.CH_2.COOH$, requires Mn, 19.25 ; C, 42.05 ; H, 3.33 ; N, 7.36 per cent].

Manganese in the complex was estimated gravimetrically as sulphate. A known weight of the substance was ignited, and the product was treated with hydrochloric acid and sulphuric acid to form manganese sulphate.

9. *Manganese-resorcylaldehyde-alanine* forms chocolate-red crystals, which are only sparingly soluble in water but fairly soluble in alcohol and pyridine. [Found : N, 4.58 ; Mn, 17.91 ; H_2O (by loss at 110°), 8.76. Mn ($C_{10}H_{11}O_5N$), 1.5 H_2O requires N, 4.56 ; Mn, 17.89 ; H_2O, 8.80. per cent]. [Found (dried at 110°) : Mn, 19.66. Calc. Mn : 19.82 per cent].

General Method of Preparation of Metal Chelate Complexes with β-Hydroxy-α-naphthaldimino Acids

The complex salts of β-hydroxy-α-naphthaldimine acids with bivalent copper, nickel, cobalt and manganese were usually obtained by the condensation of β-hydroxy-α-naphthaldehyde (1 mol.), amino-acids (1 mol.) and the corresponding metal acetate (1 mol.) in hot aqueous alcohol. The compounds of β-hydroxy-α-naphthaldehyde-anthranilic acids with different metals could also be prepared by the interaction of the Schiff's base, derived from the condensation of anthranilic acid with β-hydroxy-α-naphthaldehyde. and the metal acetates in hot alcohol. The products were purified by recrystallisation from hot aqueous alcohol containing a little pyridine.

10. *Copper-β-hydroxynaphthaldehyde-glycine* forms bluish green shining crystals, which are only sparingly soluble in water, but fairly soluble in alcohol and pyridine on warming. [Found : N, 4.55 ; Cu, 20.63 ; 'aldehyde', 55.85. Cu ($C_{13}H_{11}O_4N$) requires N, 4.54 ; Cu, 20.61 ; 'aldehyde', 55.72 per cent].

β-Hydroxy-α-naphthaldehyde in the metal chelates was estimated by following the same method as for salicylaldehyde in salicylaldimino complex compounds (Rây and Mukherjee, *loc. cit.*). The copper-β-hydroxynaphthaldoxime precipitates were dried at 100°-105° and weighed as such.

11. *Copper-β-hydroxynaphthaldehyde-anthranilate* forms light green shining crystals, sparingly soluble in water, but fairly so in alcohol and pyridine. The compound is insoluble in chloroform, benzene, toluene and acetone. [Found : N, 3.61; Cu, 16.40 ; H_2O (by loss at 110°), 4 7. Cu ($C_{18}H_{14}O_4N$), H_2O requires N, 3.60 ; Cu, 16.27 ; H_2O, 4.63 per cent] [Found (dried 110°) : Cu, 17.18. Calc. Cu : 17.16 per cent].

12. *Copper-β-hydroxynaphthaldehyde-alanine* forms greenish yellow crystals, soluble in alcohol, pyridine and dioxan. [Found : N, 4.25 ; Cu, 19.16 ; 'aldehyde', 32.05. $Cu(C_{14}H_{13}O_4N)$, 0.5 H_2O requires N, 4.22 ; Cu, 19.15 ; 'aldehyde', 31.87 per cent].

13. *Nickel-β-hydroxynaphthaldehyde-glycine* forms greenish yellow crystals, sparingly soluble in water and alcohol, but fairly soluble in pyridine on warming. [Found : N, 7.78 ; Ni, 16.32 ; 'aldehyde', 48.02. Ni ($C_{13}H_{14}O_3N_2$) requires, N, 7.76 ; Ni , 16.28 ; 'aldehyde,' 5.36 per cent].

14. *Nickel-β-hydroxynaphthaldehyde-alanine.*—The light green compound resembles the previous complex salt in properties. [Found : N, 4.18 ; Ni. 17.52 ; 'aldehyde', 51.28 ; H_2O (by loss at 108°), 5.40. $Ni(C_{14}H_{13}O_4N)$ H_2O requires N, 4.17 ; Ni, 17.49 ; 'aldehyde', 51.24 ; H_2O, 5.36 per cent].

15. *Cobalt-β-hydroxynaphthaldehyde-glycine* forms deep brown shining crystals, insoluble in water, but fairly soluble in alcohol, pyridine, acetone and dioxan. [Found : Co, 17.42 ; C, 46.06 ; H, 4.35 ; N, 4.14 ; H_2O (by loss at 138°), 10.60. Co ($C_{13}H_{11}O_4N$), 2 H_2O requires Co, 17.38 ; C, 45.83 ; H, 4.29 ; N, 4.12 ; H_2O, 10.54 per cent]. [Found (dried at 108°) : Co, 18.88. Calc. Co : 18.82 per cent].

16. *Cobalt-β-hydroxynaphthaldehyde-alanine* (reddish brown crystals) resembles the previous compound in properties. [Found : Co, 18.48 ; C, 52.08. N, 4.32 ; Co ($C_{14}H_{13}O_4N$) requires Co, 18.53 ; C, 52.81 N, 4.40 ; per cent].

17. *Manganese-β-hydroxynaphthaldehyde-glycine* forms deep brown crystals, only sparingly soluble in water but fairly in alcohol. It is insoluble in dioxan, chloroform, acetone and benzene. [Found : N, 6.59 ; Mn, 17.13 ; 'aldehyde', 52.98. $Mn(C_{13}H_9O_3N)_2.NH_2CH_2.COOH$ requires N, 6.57 ; 'Mn, 17.20 ; aldehyde', 53.86 per cent].

18. *Manganese-β-hydroxynaphthaldehyde-alanine* forms brown crystals, insoluble in water but fairly soluble in alcohol, pyridine, acetone and dioxan. [Found : Mn, 17.02 ; N, 4.36. Mn_2 ($C_{14}H_{13}O_4N$), 0.5 H_2O requires Mn, 17.01 ; N, 4.34 per cent].

19. *Schiff's Base : β-Hydroxy-α-naphthaldehyde-anthranilic acid* was prepared by the condensation of equimolecular proportions of the aldehyde and anthranilic acid in hot alcohol. It forms orange-red crystals, insoluble in water but fairly soluble in different organic solvents. It also dissolves in dilute alkalies giving a deep yellow coloured solution, but is decomposed on warming with dilute mineral acids, m. p. 236° (decomp.). [Found : C, 74.36; H, 4.58 ; N, 4.82. $(OH).C_{10}H_6CH=N.C_6H_4COOH$ requires C, 74.22 ; H, 4.47 ; N, 4.81 per cent].

Magnetic Measurements

The magnetic susceptibilities of the substances were measured in a Gouy's balance (semi-micro', single-pan 'Mettler') with a maximum field strength of 9.92×10^3 gauss. The results of measurements are tabulated below.

TABLE

Compound No.	$\chi_g \times 10^6$.	$\chi_m \times 10^6$		Temp.	μ_B (effective).
		Obs.	Corr.		
1	3.77	2217	2426	30°	1.72
2	3.83	1242	1335.3	30°	1.81
3	3.53	1186	1252	30°	1.75
4	12.85	3928	4014.2	30.2°	3.13
5	13.44	3933	4012.4	30°	3.13
6	29.40	8198	8268.5	30°	4.49
7	4.975	1766	1832.7	30.2°	2.17
8	57.74	32970	33195	30°	6.37
9	49.86	15300	15389	30°	6.13
10	4.034	1246	1313.5	30.5°	1.79
11	4.227	1643	1723	30.2°	2.05
12	3.779	1253	1334.5	30.2°	1.81
13	10.62	3831	3922.5	31°	3.06
14	8.34	2799	3134.8	30°	2.77
15	2.39	812.5	890.9	30°	1.58
16	25.9	8235	8317	30°	4.51
17	41.78	26700	26748	30°	5.72
18	34.06	11000	11081.6	30.2°	5.20

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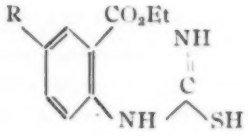
THIOPEGAN DERIVATIVES. PART VI

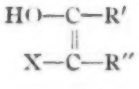
By Gurdial Mal Sharma, I. Sen Gupta and K. S. Narang

Several 10 : 11-thiopegan derivatives have been synthesised and the structure of one of the two compounds, obtained by condensation of 2-carbethoxyphenylthiourea with monochloroacetone, has been established.

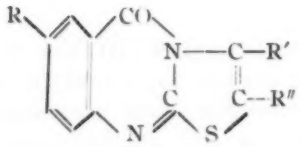
Narang *et al.* (*J. Sci. Ind. Res.*, 1953, **12B**, 466 ; *Res. Bull. East Panjab Univ.*, 1953, **36**, 143 ; this *Journal*, 1954, **31**, 848) obtained thiopegan derivatives by the condensation of 2-carbethoxyphenylthiourea or its 4-methyl derivative (I) with various α-haloketones (II), and assigned to them the tentative structure of 10 : 11-thiopegan derivatives (III) though the structure (IV) of 9 : 10-thiopegan derivatives was also considered as possible.



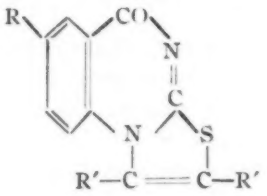
(I)



(II) [R′, R″ = H or other groups; X = halogen]



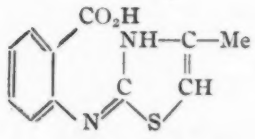
(III)



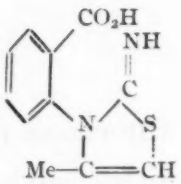
(IV) [R = H or Me]

In majority of the cases condensations of (I) with (II) gave rise to only one product in each case, but the condensation of (I, R = H) with monochloroacetone gave rise to two isomeric compounds (m. p. 179° and 302°) (*J. Sci. Ind. Res.*, 1953, **12B**, 469). These compounds evidently had the structures (III) and (IV) (R = R″ = H; R′ = Me) but the assignment of the particular structure to each of the two isomers was then not possible.

The compound of m. p. 179°, on alkaline hydrolysis gave rise to a product which had been characterised as 2 : 4-dihydroxyquinazoline or 2 : 4-diketotetrahydroquinazoline, and the alkaline hydrolysis of the compound of m.p. 302° afforded a product, the analytical values for which agreed with those of the initial hydrolytic products (V or VI) which one could expect from (III) or (IV) respectively (R = R″ = H and R′ = Me in each case).



(V)



(VI)

The hydrolytic degradation therefore did not lead to any confirmatory evidence regarding the structure of the two compounds.

Condensation of anthranilic acid with 2-chloro-4-methylthiazole afforded a product which was identical with the product of m.p. 179°, mentioned above. This product therefore has the structure (III : R, R″=H; R′=Me). It is therefore concluded that the higher melting product (m.p. 302°) may have the angular structure (IV : R=R″=H; R′=Me).

Anthranilic acid on condensation with 2-chloro-4 : 5-dimethylthiazole and 2-chloro-4-methyl-5-carbethoxythiazole furnished products (m. p. 172° and 132°), evidently possessing the linear structure (III). These compounds were found to be different from the condensation products of (I, R = H) with (II : R′=R″= Me ; R′= Me; R″=CO_2Et respectively) which melted at 281° and 194° (*J. Sci. Ind. Res.*, 1953, **12B**, 469). These may therefore be assigned the angular structure (IV) with respective values for R, R′ and R″. These angular structures, however, need further confirmation through unambiguous synthesis.

Experimental

Hydrolysis of the Lower-melting Condensation Product of (I, R=H) *with Monochloroacetone* (m. p. 179°).—A solution of the compound (2 g.) in 125 c. c. of 5% alcoholic KOH was refluxed for 5 hours. The solvent was removed at 50°-60° in vacuum and the residue dissolved in 35 c. c. of water. After clarification with charcoal the filtrate was made just acidic with acetic acid. The precipitate was collected and crystallised from ethanol as colorless needles, m. p. 350° (with slight shrinkage at 340°). This compound did not contain sulphur, and admixture with 2 : 4-dihydroxyquinazoline (Bogert, *J. Amer. Chem. Soc.*, 1916, **38**, 612) did not depress the m. p.

Hydrolysis of the higher-melting condensation product of (I, R=H) *with monochloroacetone* (m. p. 302°) was carried out in the same way as above. The product was crystallised from 10% ethanol in colorless needles, m. p. 190°, yield 1.6 g. from 2 g. [Found : N, 11.7. $C_{11}H_{10}O_2N_2S$ (*i. e.*, for V or VI) requires N, 11.92 per cent].

Synthesis of (III : R=R″=H ; R′=Me).—A mixture of anthranilic acid (1 g.) and 2-chloro-4-methylthiazole (1 g.) (Tcherniac, *J. Chem. Soc.*, 1919, **115**, 1071) was heated in an oil-bath. The reaction mixture slowly became liquid and the reaction which had started at 130° became vigorous at 140°. After heating at 140°-150° for 5 minutes the temperature was raised to 160-70° for half an hour when the mixture became solid. The insoluble residue, obtained after basification with sodium carbonate solution, on crystallisation from dilute ethanol furnished colorless needles, m. p. 179°, yield 1.3 g.

Admixture of this with lower melting condensation product of (I, R=H) with monochloracetone did not depress the m. p.

Synthesis of (III : R=H, R′=R″=Me).—A mixture of anthranilic acid (0.7 g.) and 2-chloro-4 : 5-dimethylthiazole (1 g.) (Ganapathi and Venkataraman, *Proc. Ind. Acad. Sci.*, 1945, **22A**, 362) was heated in an oil-bath. The mixture liquefied at 120° and after a vigorous reaction at 130°-140° became solid during five minutes. The temperature was raised to 150° for half an hour. The product after basification with sodium carbonate solution was crystallised from ethanol in colorless needles, m. p. 172°, yield 0.9 g, (Found : N, 12.0 ; S, 13.67. $C_{12}H_{10}ON_2S$ requires N, 12.17 ; S, 13.91 per cent).

Synthesis of (III : R=H, R′=Me, R″=CO_2Et) was effected as in the above case from anthranilic acid (1.37 g.) and 2-chloro-4-methyl-5-carbethoxythiazole (2 g.) (Ganapathi and Venkataraman, *loc. cit.*). The product was crystallised from ethanol in light pale needles, m. p. 132°, yield 2.4 g. (Found: C, 58.45 ; H, 3.9. $C_{14}H_{12}O_2N_2S$ requires C, 58.3 ; H, 4.1 per cent).

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BROMINATION OF THE SUBSTITUTED AMIDES OF CYANOACETIC ESTER

By M. N. Desai

Bromination of substituted amides of cyanoscetic ester has been investigated and it has been observed that bromine replaces preferentially the hydrogen atom of the methylene group in the case of majority of amides, and in few cases it enters the nucleus, and not the side-chain.

West (*J. Chem. Soc.*, 1922, **121**, 2196) investigated the action of bromine on *sym.*-disubstituted aromatic amides of malonic acid, and found that the hydrogen atom in the *para* position in the phenyl group and one of the hydrogen atoms in the methylene group of the malonyl radical were equally susceptible to the attack of bromine and that the substitution of bromine for hydrogen in chloroform or acetic acid solution only took place in the methylene group of the malonyl radical of *sym.*-tetra-substituted amides.

The present communication is aimed at investigating the effect of bromination on the substituted amides of cyanoacetic ester on the similar line. Bromination, however, was observed to take place in acetic acid and not in chloroform. The amides selected were : (1) cyanoacetbenzylamide, (2) cyanoacet-*p*-tolylamide, (3) cyanoacet *o*-tolylamide, (4) cyanoacet-*o*-chloroanilide, (5) cyanoacet-*m*-chloroanilide, (6) cyanoacet-*p*-anisidylamide, (7) cyanoacet-*m*-xylylamide, (8) cyanoacet-*o*-anisidylamide, (9) cyanoacet-*p*-phenetidylamide, (10) cyanoacet-*o*-phenetidylamide, (11) cyanoacet-*m*-tolylamide, (12) cyanoacet-α-naphthylamide, (13) cyanoacet-β-naphthylamide. Of the above amides, numbers 8, 9 and 10 are new.

With one mole of bromine it has been found that only one bromine atom replaces the hydrogen atom of the methylene group of the amides No. 1-10, but with No. 11 and 12 it is found to enter the nucleus and not in the side-chain. With two moles of bromine, however, it has been found that with cyanoacet-*o*-tolylamide, bromine not only replaces the side-chain hydrogen but also enters the nucleus in the *para* position to the $-NH_2$ group. With amides No. 11 and 12, one bromine atom replaces the hydrogen of the nucleus, while the second replaces the hydrogen of the side-chain. With amide No. 13, one mole of bromine affords a mixture of products, but with two moles of bromine a product having one bromine in the side-chain and the other in the nucleus is obtained.

Experimental

Preparation of the Substituted Amides of Cyanoacetic Ester.—Aromatic amine (0.2 *M*) and cyanoacetic ester (0.2 *M*) were heated together in a round-bottomed flask with an air condenser in an oil-bath at 160°-170° for 7 hours. The content was transferred in water, the product filtered on the filter pump and dried. It was washed with a mixture of benzene and petroleum ether to remove the unchanged amine. On charcoal-

ing the product with alcohol, acetic acid etc., crystalline product was obtained. The details of the experiments are shown in Table I.

TABLE I

Cyanoacet-arylamides.

	Name	Crystallised from.	M. P.	Formula.	% Nitrogen Found.	% Nitrogen Calc.
1.	*o*-Phenetidyl	Dil. acetic acid	112-13°	$C_{11}H_{12}O_2N_2$	13.81	13.72
2.	*p*-Phenetidyl	Alcohol	175-77°	$C_{11}H_{12}O_2N_2$	13.79	13.72
3.	*o*-Anisidyl	Dil alcohol	126-28°	$C_{10}H_{10}O_2N_2$	14.81	14.73

Preparation of Bromo Compounds of the Substituted Amides of Cyanoacetic Ester.—The amide (0.01 *M*) was dissolved in 10 to 15 c. c. of glacial acetic acid and bromine (0.01 *M*) in acetic acid (20% solution of bromine in acetic acid) was added to the hot solution gradually with shaking. The flask with the content was left overnight. On the next day it was transferred to an evaporating dish and left to evaporate for 2 to 4 days. The product was washed with a mixture of benzene and petroleum ether and was crystallised from alcohol, benzene or the mixture of benzene-alcohol.

TABLE II

Cyanoacetmonobromoarylamides.

	Name.	Crystallised from.	M. P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.	% Bromine. Found.	% Bromine. Calc.
1.	Benzylamide	Alcohol-benzene	150-51°	$C_{10}H_9ON_2Br$	11.32	11.07	31.60	31.62
2.	*p*-Tolyl ,,	Do	186°	$C_{10}H_9ON_2Br$	11.24	11.07	30.72	31.62
3.	*o*-Tolyl ,,	Do	189-91°	$C_{10}H_9ON_2Br$	11.42	11.07	30.90	31.62
4.	*o*-Chloroanilide	Benzene	171-73°	$C_9H_6ON_2BrCl$	10.38	10.23	28.90	29.20
5.	*m*- ,,	Benzene-alcohol	170-72°	Do	10.47	10.23	30.00	29.20
6.	*o*-Anisidyl amide	Benzene	163-65°	$C_{10}H_9O_2N_2Br$	10.57	10.41	28.47	29.70
7.	*p* Anisidyl ,,	Alcohol	183-85°	Do	10.27	10.41	28.9	29.7
8.	*m*-Xylyl ,,	Benzene-alcohol	171-72°	$C_{11}H_{11}ON_2Br$	10.22	10.48	30.0	29.9
9.	*p*-Phenetidyl ,,	Do	187-89°	$C_{11}H_{11}O_2N_2Br$	9.92	9.89	28.4	28.2
10.	4-Bromo-*m*-tolyl ,,	Do	189-91°	$C_{10}H_8ON_2Br_2$	8.61	8.43	24.45	24.12
11.	5-Bromo-*o*-tolyl ,,	Do	192-93°	Do	8.57	8.43	25.42	24.12
12.	4-Bromo-α-naphthyl ,,	Benzene	194-95°	$C_{13}H_8ON_2Br_2$	7.73	7.61	22.09	21.73
13	1-Bromo-β-naphthyl ,,	Do	193-95°	Do	7.68	7.61	22.47	21.73
14.	4-Bromo-*m*-tolyl ,,	Benzene-alcohol	155°	$C_{10}H_9ON_2Br$	12.13	11.07	31.83	31.6
15.	4-Bromo-α-naphthyl ,,	Do	214-15°	$C_{13}H_9ON_2Br$	9.82	9.68	27.47	27.68

The bromine in the side-chain of compounds 1-13 was estimated by Volhard's method.

In the case of dibromo derivatives, 0.02 *M* of bromine was employed. The position of bromine in the nucleus was found by decomposing the bromo derivatives with hot KOH solution, and identifying the bromoamines. The details are shown in Table II.

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REACTIONS OF HYPONITRITES. PART V. THE ACTION OF CHARCOAL ON CALCIUM NITRITE

By Trambaklal Mohanlal Oza and Vasantrai Trambaklal Oza

A careful study has shown that the dissociation of calcium nitrite starts much earlier than thought before as, at 280°, it is found to react with charcoal. Calcium hyponitrite is found in the reaction products, and it appears that in the action of carbon dioxide on calcium hyponitrite, nitrous oxide is displaced ; the presence of moisture in the system plays an important role, little displacement of nitrous oxide occurring when the system is dry.

The action of charcoal on calcium nitrite does not appear to have been studied in the past. During his experiments on the action of charcoal on potassium nitrite (Oza and Shah, this *Journal*, 1943, **20**, 261) Oza observed the presence of nitrous oxide in the gas (*loc.cit.*, foot note, p. 267) and a systematic work on the action of charcoal on sodium nitrite (Oza, *ibid.*, 1944, **21**, 71) revealed the presence of considerable amounts of the gas in the products. This was explained as due to occurrence of consecutive reactions:

$$2NaNO_2 + C \rightarrow Na_2N_2O_2 + CO_2 \quad \ldots \quad (1)$$

$$Na_2N_2O_2 + CO_2 \rightarrow Na_2CO_3 + N_2O \quad \ldots \quad (2)$$

Dwivedi (M. Sc. thesis, Bombay Univ., 1948) carried out experiments on the action of charcoal on barium nitrite but did not seem to have tested for the formation of the hyponitrite in the solid, or nitrous oxide in the gaseous products of the reaction.

The action of charcoal on calcium nitrite has a bearing on the action of carbon dioxide on the hyponitrites (eq. 2), and this has a bearing on the structure of hyponitrites. The action of charcoal on calcium nitrite has therefore been carefully examined in order to find out the effect, if any, of the moisture present in the system on the production of nitrous oxide.

As regards the action of carbon dioxide on hyponitrites, Divers (*J. Chem. Soc.*, 1899, **47**, 97) reported no action on calcium hyponitrite tetrahydrate and Thum (*Monatsh.*, 1893, **14**, 294) reported no action on silver hyponitrite. Partington and Shah (*J. Chem. Soc.*, 1931, 2071; 1932, 2589) found no change in weight of sodium hyponitrite or alkaline earth hyponitrites in air, though the former got spoiled in a fortnight. Kirschner (*Z. anorg. Chem.*, 1898, **16**, 424) found that barium hyponitrite was decomposed by carbon dioxide.

In the present work the action of charcoal on calcium nitrite has been studied in vacuo with a view to finding out if (*i*) hyponitrite is produced in the reaction, (*ii*) nitrous oxide is present in the gaseous products, and (*iii*) the production of nitrous oxide, if any, is influenced by the presence of moisture in the system. Moisture is likely to have an important influence (vide Oza and Oza, *J. Chem. Soc.*, 1953, 909). Hyponitrite is found in the residue after Oza (*loc. cit.*, p. 72) while nitrous oxide is also

found present. The influence of moisture has been tested for by carefully dehydrating, as far as possible, the nitrite in vacuo in a dry system containing P_2O_5. P. C. Ray (*J. Chem. Soc.*, 1905, **87**, 177) showed that $Ca(NO_2)_2,H_2O$ lost about half of its water of crystallisation, when heated. It is found that about 3/4ths of the water molecule can be got rid of under suitable conditions.

EXPERIMENTAL

$Ca(NO_2)_2,H_2O$ was the same as that used by Oza and Oza (*loc. cit.*) and charcoal was the ashless quality (Oza, *loc. cit.*). Nitrogen dioxide was absorbed out along with its equivalent of nitric oxide in the KOH trap in the apparatus (modified form of that used by Oza and Oza, *loc. cit.*) and was determined as

$$2KOH + N_2O_3 = 2KNO_2 + H_2O.$$

Absorbents used in the analyses were all saturated with such of the gases present as not meant for them. Carbon dioxide was absorbed out first and then nitric oxide in alkaline sulphite, end-point being tested with ferrous sulphate. Nitrous oxide was absorbed out in cold alcohol, saturated with carbon monoxide, and carbon monoxide in ammoniacal cuprous chloride. The recorded volumes are at N.T.P. except otherwise stated.

The solids in the residue were repeatedly treated with water till filtrate was not alkaline and the solution titrated out immediately for CaO with succinic acid. Nitrite and nitrate were determined as usual. The insoluble residue, dissolved in HCl, was precipitated as oxalate and calcium found was calculated as $CaCO_3$.

Procedure.—The system, tested for leak, containing weighed amounts of the constituents was heated electrically, temperature being maintained constant to within $\pm 5^\circ$ by a rheostat. The results recorded in Table 1 show that (*i*) no nitrate is formed except at 410° in 4 hours, with a low proportion of charcoal showing that the oxides of of nitrogen, dioxide in particular, react more or less completely with charcoal in preference to calcium oxide ; (*ii*) oxide and carbonate are present at all temperatures and with all masses of charcoal ; (*iii*) gas contains nitrous oxide in all experiments, the relative production being the least in the violent experiment (No. 4) at 490° and the greatest in the slow experiment (No. 2) at 290° with 25% charcoal; (*iv*) nitric oxide is the major component of the gaseous products and nitrogen is present ; (*v*) free carbon dioxide is very small and as considerable quantities of carbonate are present, this shows that carbon dioxide is very effectively fixed up ; (*vi*) the quantities of nitrogen dioxide in the gas are very small.

An experiment (*vide infra*) was performed with great care : 0.2020 g. of $Ca(NO_2)_2$, H_2O was placed in the system containing P_2O_5 in the bulb in place of the usual KOH lye. The system was evacuated and the temperature maintained at 80° for 4 hours, at the end of which the substance was carefully weighed (*ca.* 0.1844 g.). The system was again fitted up, evacuated and heated for one hour and weighed; the weight remained the same. The temperature was then raised to 150° and kept constant for 2 hours after which, on weighing, the weight was again found to be the same. No gas was

evolved and the vacuum of the system remained unaffected. The loss of weight was thus 0.0176 g. Loss of $\frac{1}{2}H_2O$ should cause a loss of weight of 0.01212 g. and loss of $\frac{3}{4}H_2O$, 0.01825 g. Temperature was then slowly raised to 280° when gas was evolved and mercury of the pump showed trailing by nitrogen dioxide formed in the system. The first portion of the gas collected was 4.5 c.c. at 32°/758 mm. This was found to consist of 1.3 c.c. of CO_2, 2.9 c.c. of NO and 0.3 c.c. of N_2 (nitrous oxide was not tested for). At this stage the temperature was lowered to room temperature and the system left over P_2O_5 for two days. On the third day the temperature was raised to 200°, maintained there for 2 hours and then slowly raised; at 220° some gas was evolved but was very slight and the action soon ceased; regular action began at 290° when 4.55 c.c. of gas was collected in 4 hours at 32°/758 mm. This gas contained no CO_2, 4.35 c.c. of NO and 0.2 c.c. of N_2 with only a trace of N_2O. Temperature was then raised to 350° when 2.4 c.c. of gas was collected in 40 minutes which contained 2.05 c.c. of NO, no N_2O and 0.35 c.c. of N_2. Finally the temperature was raised to 400° when in 1½ hours 26.2 c.c. of gas was given off at 32°/758 mm. of which 16.7 c.c. was NO, less than 0.1 c.c. was nitrous oxide, 0.9 c.c. was CO and the rest 8.5 c.c. was N_2. The apparatus was then allowed to cool and the residue moistened with 1.5 c.c. of water and the moistened residue heated in a water-bath for ½ hour, the tap between the P_2O_5 column and heating column being closed in the mean while. On opening the tap, the mercury column of the pump fell showing the presence of gas in the system. The gas was pumped off: it measured 0.4 c.c. all of which, leaving a trace, was absorbed out in cold alcohol.

TABLE I

Action of charcoal on calcium nitrite.

Expt No.	Temp.	Time.	Mass (g.)		Composition of residue (g.)					Gaseous products. (in c.c.)					
			$Ca(NO_2)_2$, H_2O.	Charcoal.	$Ca(NO_2)_2$.	$Ca(NO_3)_2$.	$CaCO_3$.	CaO.	$Ca(NO_2)_2$ consumed.	CO_2.	NO.	N_2O.	CO.	N.	NO_2
1	410°	4	0.2010	0.0200	0.0257	0.0435	0.0584	0.0168	0.1511	0.2	26.9	0.8	1.1	6.8	0.0
2	290°	1 *	0.2029	0.0507	0.1480	Nil	0.0082	0.0084	0.0305	0.0	3.0	1.8	0.3	2.0	0.2
3	410°	1	0.2004	0.0491	0.0157	,,	0.0702	0.0285	0.1600	0.0	19.3	4.0	1.2	11.3	0.3
4	490°	**	0.2020	0.0850	0.0462	,,	0.0687	0.0190	0.1276	0.0	26.3	0.5	0.9	5.8	0.5

* Charcoal intimately mixed by grinding the reactants together in a mortar.

** Reaction was very vigorous.

DISCUSSION

The above results show that production of carbon dioxide occurs at 280° at the start of the reaction. The decomposition of calcium nitrite was noticed at 360° (Oza and Oza, *loc. cit.*) although Addison and Lewis (*J. Chem. Soc.*, 1953, 1874) quoted it to be 230°. The present observation therefore seems to confirm the view that the initial stage in the decomposition of the nitrite is that of dissociation: the latter, being

a continuous process, is inappreciable at low temperatures but becomes appreciable at higher ones. The oxides of nitrogen, released as

$$Ca(NO_2)_2 \rightleftharpoons CaO + NO + NO_2,$$

then react with the charcoal present in the system to form carbon dioxide ; free carbon dioxide is present at the start when little CaO is present in the system.

The results of the present work show also that complete dehydration of calcium nitrite monohydrate without decomposition is not possible though about three-fourths of the water molecule can be expelled.

The most important results are, perhaps, the observations that (*i*) calcium hyponitrite is formed from calcium nitrite by the reducing action of charcoal at a comparatively early temperature (280°) when the dissociation of the nitrite is not appreciable ; (*ii*) the hyponitrite, so formed, is fairly stable in the system if the latter is dry, for it shows its presence even after the system is heated at 400° for $1\frac{1}{2}$ hours : the usual temperature of decomposition of $CaN_2O_2,4H_2O$ is 330° and earlier (Oza and Oza, *loc. cit.*) ; and (*iii*) carbon dioxide displaces nitrous oxide from calcium hyponitrite in an ordinary system but does not seem to do so in a perfectly dry system.

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CHLORAMINE-B AS A BROMOMETRIC REAGENT. PART I

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Chloramine-B has been used in conjunction with KBr as a bromometric reagent instead of $KBrO_3$ in acidic medium

Use of chloramine-B as a volumetric oxidising agent, where the solutions are directly titrated, has already been reported by one of us (*Res. Bull. East Panjab Univ.*, 1954, Nos. 41, 43, 44; this *Journal*, 1954, **31**, 327). In the present investigation chloramine-B in conjunction with potassium bromide has been used as a bromometric reagent in acidic medium in place of potassium bromate. The bromine required for bromination is obtained according to the following reaction :

$$C_6H_5SO_2N(Na)Cl + 2KBr + 2HCl \longrightarrow C_6H_5SO_2NH_2 + NaCl + 2KCl + Br_2.$$

Potassium bromide is taken in excess to ensure complete reduction of chloramine-B and to increase the solvent power of the solution for bromine.

It has been found that the nascent bromine liberated in the solution reacts with the substances as follows :

1.	$As_2O_3 + 2Br_2 + 2H_2O$	$\longrightarrow As_2O_5 + 4HBr.$
2.	$Sb_2O_3 + 2Br_2 + 2H_2O$	$\longrightarrow Sb_2O_5 + 4HBr.$
3.	$SnCl_2 + 2HCl + Br_2$	$\longrightarrow SnCl_4 + 2HBr.$
4.	$N_2H_4 + 2Br_2$	$\longrightarrow N_2 + 4HBr$
5.	$2FeSO_4 + H_2SO_4 + Br_2$	$\longrightarrow Fe_2(SO_4)_3 + 2HBr.$
6.	$H_2SO_3 + H_2O + Br_2$	$\longrightarrow H_2SO_4 + 2HBr.$
7.	$H_2S + 4Br_2 + 4H_2O$	$\longrightarrow H_2SO_4 + 8HBr.$
8.	$ThCl + 2HCl + Br_2$	$\longrightarrow ThCl_3 + 2HBr.$
9.	$KCNS + 4H_2O + 4Br_2$	$\longrightarrow CNBr + KHSO_4 + 7HBr.$
10.	$2K_4[Fe(CN)_6] + Br_2$	$\longrightarrow 2K_3[Fe(CN)_6] + 2KBr.$
11.	$KCN + Br_2$	$\longrightarrow CNBr + KBr.$
12	$K_2SO_3 + H_2O + Br_2$	$\longrightarrow K_2SO_4 + 2HBr.$
13.	$Na_2S_2O_3 + 5H_2O + 4Br_2$	$\longrightarrow Na_2SO_4 + H_2SO_4 + 8HBr.$
14.	$Na_2S_4O_6 + 10H_2O + 7Br_2$	$\longrightarrow Na_2SO_4 + 3H_2SO_4 + 14HBr.$
15.	$Na_2S + 4H_2O + 4Br_2$	$\longrightarrow Na_2SO_4 + 8HBr.$

In the case of potassium sulphocyanide and potassium cyanide, the cyanide group is oxidised to bromocyanogen, which is in conformity with the observation of Oberhauser (*Z. anorg. Chem.*, 1925, **144**, 257). In the estimation of potassium ferrocyanide, the excess of bromine was reduced immediately with arsenious acid to prevent bromination of the cyanide group.

Sodium thiosulphate, tetrathionate and sulphides are all directly oxidised to sulphate. Iodine, which is very commonly used as an oxidising agent, oxidises thiosulphate to tetrathionate, while tetrathionates are stable to this reagent. Sulphides, H_2S, etc. are only oxidised to sulphur by it (Scott, "Standard Methods of Chemical Analysis", 1939, Vol. I, p. 914) while permanganates etc. furnish a variety of products. Here, in this procedure all the sulphur compounds are quantitatively oxidised to sulphate.

Three different procedures have been employed to determine the end-point of these titrations:

(*a*). Starch iodide solution as an indicator.

(*b*). 1 c.c. of saturated potassium bromide solution.

(*c*). 2-3 drops of 0.2% indigo carmine solution.

Direct Titration Method.—(*a*). Known weights of A.R. substances were dissolved in 100 c.c. of water in conical flasks if pure solids were not available; the solutions of these substances were standardised by already known method. To it was added 2 c.c. of starch solution and a small crystal of potassium iodide. The solution was titrated against standard chloramine-B solution from a burette, slowly, with constant shaking until a permanent blue colour just appeared. The determinations of arsenious oxide, tartar emetic and hydrazine sulphate were done in the presence of excess of sodium bicarbonate solution. The results of the various titrations are recorded in Table I.

TABLE I

Arsenious oxide.		Tartar emetic.			
0.098 *N*-C.B used.	Taken.	Found.	0.098 *N*-C.B used.	Taken.	Found.
10.30 c.c.	0.0499 g.	0.0499 g.	10.70 c.c.	0.1780 g.	0.1753 g.
14.30	0.0699	0.0694	13.70	0.2281	0.2243
20.30	0.0999	0.0985	17.00	0.2766	0.2783
22.30	0.1089	0.1082	19.10	0.3157	0.3127

$SnCl_2.2H_2O$.			Hydrazine sulphate.			Sulphurous acid.		
0.108 *N*-C.B. used.	Taken.	Found.	0.108 *N*-C.B. used.	Taken.	Found.	0.105 *N*-C.B used.	Taken	Found.
6.80 c.c.	0.0846 g.	0.0829 g	9.30 c.c	0.0325 g.	0.0326 g.	13.40 c.c	0.05820 g.	0.0768 g.
8.80	0.1099	0.1073	12.00	0.0423	0.0421	19.00	0.08125	0.08179
10.90	0.1353	0.1328	16.00	0.0563	0.0562	22.80	0.10050	0.09815
12.95	0.1607	0.1579	15.05	0.0528	0.0528	30.90	0.13200	0.13302

(*b*). To the aqueous solution of the substance in a conical flask were added 10 c.c. of 10% potassium bromide, 10 c.c. of concentrated hydrochloric acid, 2-3 drops of 0.20% indigo carmine, and the mixture diluted to 100 c.c. A standard chloramine-B solution was very slowly run in with constant stirring until the blue colour of the indigo carmine was discharged. In certain titrations no indicator was used, the end of the titration was reckoned by the appearance of a yellow colour due to the liberation of bromine. The results are recorded in Tables II and III respectively.

TABLE II

Arsenious oxide.			Tartar emetic.		
0.098 *N*-C.B. used.	Taken.	Found.	0.098 *N*-C.B. used.	Taken.	Found.
10.30 c.c.	0.0499 g.	0.0499 g.	10.70 c.c.	0.1780 g.	0.1753 g.
14.50	0.0699	0.0703	13.80	0.2281	0.2259
20.50	0.0999	0.0994	17.10	0.2766	0.2793
22.50	0.1089	0.1091	19.20	0.3157	0.3145
Stannous chloride.			**Hydrazine sulphate.**		
0.108 *N*-C.B. used.	Taken.	Found.	0.108 *N*-C.B. used.	Taken.	Found.
6.90 c.c.	0.0846 g.	0.0841 g.	9.50 c.c.	0.0325 g.	0.0333 g.
11.65	0.1438	0.1420	12.00	0.0423	0.0421
13.70	0.1692	0.1670	15.50	0.0553	0.0544
15.90	0.1946	0.1938	19.60	0.0683	0.0687
Thallous chloride.			**Sulphurous acid.**		
0.105 *N*-C.B. used.	Taken.	Found.	0.105 *N*-C.B. used.	Taken.	Found.
6.05 c.c.	0.0760 g.	0.0762 g.	13.50 c.c.	0.0585 g.	0.0581 g.
10.80	0.1373	0.1361	17.60	0.0759	0.0757
13.80	0.1730	0.1738	23.00	0.0999	0.0990
			31.10	0.1340	0.1338

TABLE III

Arsenious oxide.			Tartar emetic.		
0.098 *N*-C.B. used.	Taken.	Found.	0.098 *N*-C.B. used.	Taken.	Found.
10.30 c.c.	0.0499 g.	0.0499 g.	10.60 c.c.	0.1780 g.	0.1753 g.
14.50	0.0699	0.0703	13.80	0.2281	0.2250
20.50	0.0999	0.0994	17.10	0.2766	0.2799
22.50	0.1089	0.1099	19.20	0.3157	0.3143
Stannous chloride.			**Hydrazine sulphate.**		
0.108 *N*-C.B. used.	Taken.	Found.	0.108 *N*-C.B. used	Taken.	Found.
6.90 c.c.	0.0846 g.	0.0841 g.	9.40 c.c.	0.0325 g.	0.0331 g.
11.65	0.1438	0.1420	12.20	0.0424	0.0425
13.00	0.1607	0.1585	16.70	0.0585	0.0586
			21.40	0.0748	0.0751
Sulphurous acid.			**Thallous chloride.**		
.105 *N*-C.B. used	Taken.	Found.	0.105 *N*-C.B. used.	Taken.	Found.
13.60 c.c.	0.0586 g.	0.0586 g.	6.00 c.c.	0.0758 g.	0.0755 g.
17.60	0.0753	0.0758	9.20	0.1160	0.1159
23.10	0.0990	0.0994	13.70	0.1730	0.1726

General Procedure for the Excess Method.—The titrations here recorded were carried out in a flask similar to that used by Mayr and Peyfuss (*Z. anorg. Chem.*, 1915, **92**, 127). Procedure adopted was the same as in a previous paper by A. Singh (this *Journal*, 1954, **31**, 327, 328).

A measured sample of the solution was placed in a half-litre flask and from the volume of chloramine-B used, the amount of each substance was calculated. The results are recorded in Table IV.

TABLE IV

Tartar emetic.			Stannous chloride.		
0.098 *N*-C B used.	Taken.	Found.	0 108 *N*-C B used.	Taken.	Found.
10 40 c.c.	0.1700 g.	0 1702 g	7.00 c.c.	0.0846 g.	0.0853 g.
13.50	0.2250	0.2210	8.90	0.1099	0.1085
16.40	0.2680	0 2685	11 50	0 1438	0.1402
21 85	0 3577	0 3577	13.80	0.1692	0 1682

1 c.c. of 0 098 *N*-C.B ≡0.001637 g. tartar emetic. 1 c.c. of 0.108*N*-C.B.≡0.01219 g. $SnCl_2, 2H_2O$.

Hydrazine sulphate.			Ferrous sulphate		
0.108 *N*-C.B. used.			0.1 *N*-C B. used.		
12.00	0.0423	0 0422	10.05	0.2780	0 2919
9 50	0.0325	0 0333	13 00	0.3614	0 3614
15.05	0.0528	0.0528	16.90	0.4726	0.4698
19.40	0.0683	0.0681	21.00	0 5838	0.5838

1 c.c of 0.108*N*-C.B ≡0 00351 g. $N_2H_4.H_2SO_4$ 1 c.c. of 0.1 *N*-C.B.≡0.0278 g. $FeSO_4, 7H_2O$

Sulphurous acid.			Hydrogen sulphide.		
0.105 *N*-C.B. used.			0 1 *N*-C.B. used.		
13.60	0.0586	0.0586	15.35	0.0066	0.0065
17.50	0 0757	0.0753	22 40	0 0098	0.0095
24 30	0.1120	0 1046	18.20	0.0077	0.0077
31.00	0.1343	0.1335	20.40	0.0087	0.0086

1 c.c. of 0.105 *N*-C.B.≡0.004305 g. H_2SO_3. 1 c.c. of 0.1 *N*-C B.≡0.000425 g. H_2S

Thallous chloride			Potassium sulphocyanide.		
0.105 *N*-C.B. used.			0.108 *N*-C.B. used		
12.60	0.1600	0.1587	12.20	0.0160	0.0160
10.90	0.1380	0 1374	14.70	0.0192	0.0193
10.70	0.2500	0.2482	23.30	0 0304	0.0305
12 20	0 1528	0 1537	19 80	0.0256	0 0260

1 c.c. of 0 105 *N*-C.B.≡0 0126 g. ThCl. 1 c c of 0.108 *N*-C.B.≡0.00131 g KCNS.

Potassium ferrocyanide.			Potassium cyanide.		
0 1 *N*-C.B. used.			0.098 *N*-C.B. used.		
9.95	0.4220	0.4199	7.70	0 0250	0 0245
14.00	0 5908	0 5908	10.00	0.0322	0.0319
16 90	0 7124	0 7132	13.10	0.0421	0.0417
20.00	0 8440	0 8440	14.60	0 0497	0.0465

1 c.c. of 0 1 *N*-C B ≡0 0422 g. $K_3Fe(CN)_6, 3H_2O$. 1 c c. of 0 098 *N*-C B.≡0.0003185 g. KCN.

Potassium sulphite.			Sodium thiosulphate.		
0.1 *N*-C B. used.			0.1 *N*-C.B. used.		
12.50	0.0980	0.0987	10.20	0.0310	0 0317
15.10	0.1185	0 1193	17 00	0.0528	0.0528
16.50	0 1296	0.1304	21.20	0 0652	0.0659
23.20	0.1817	0.1833	23.10	0 0716	0 0717

1 c.c. of 0.1 *N*-C B.≡0 0079 g. K_2SO_3≡0 003103 g. $Na_2S_2O_3, 5H_2O$.

Sodium tetrathionate.			Sodium sulphide.		
8.50	0.0165	0 0164	13.20	0.0128	0.0128
13.70	0 0264	0.0264	9.00	0 0086	0 0087
16.20	0.0309	0 0313	17.20	0.0164	0.0167
11.00	0.0212	0.0213	30.40	0.0294	0.0296

1 c.c. of 0.1 *N*-C.B.≡0.001929 g. $Na_2S_4O_6$≡0 000975 g. Na_2S.

On comparing the results obtained from the various methods it is clear that the excess method is of wide application and, moreover, affords very accurate results. The direct method though appears to be simple does not produce very accurate results because in some cases the end-point is not very sharp and high results are generally obtained. In the opinion of the author the excess method should always be preferred, wherever possible, over the direct method.

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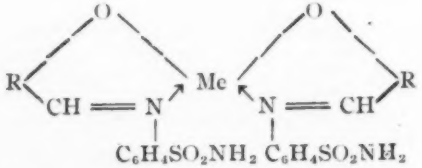
INNER-METALLIC COMPLEX SALTS OF OXYALDIMINES WITH POLYCYCLIC RINGS

By Ajit Kumar Mukherjee and Priyadarajan Rây

Several inner-metallic complexes of bivalent copper, nickel, cobalt, manganese and of sexivalent uranium with *o*-hydroxyaldehydes and sulphanilamide, *o*-phenylenediamine or ethylenediamine, have been prepared and their properties studied. Possible structures of the compounds have also been suggested from a study of their magnetic susceptibilities

The products formed by the action of metallic salicylaldehyde upon ammonia, different amines and related compounds present an interesting chapter in the study of metal chelate compounds (Pfeiffer *et al.*, *J. prakt. Chem.*, 1931, **129**, 163 ; 1936, **148**, 243 ; 1937, **149**, 217 ; *Ber.*, 1944, **77A**, 59 ; Calvin *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 2254, 2263, 2273). Similar metal chelate complexes of copper, nickel, cobalt, iron, manganese, uranium and vanadium with *o*-hydroxyaldehydes and different amino-acids or glycine hydroxamic acid were prepared and studied by us (this *Journal*, 1950, **27**, 707; 1955, **32**, 493). In the present paper, the preparation and properties of a series of metallic chelate complexes of salicylaldehyde, resorcylaldehyde or β-hydroxynaphthaldehyde with sulphanilamide, *o*-phenylenediamine and ethylenediamine have been described. The magnetic susceptibilities of the complexes, described here, were measured with a view to determining their structure and the nature of the bond involved in their formation.

The compounds were obtained as usual by the interaction of *o*-hydroxyaldehydes, amines and the corresponding metal acetates in hot aqueous alcoholic medium. The metal chelate complexes of salicylaldehyde, resorcylaldehyde or β-hydroxynaphthaldehyde with *p*-aminophenylsulphonamide (sulphanilamide) behave like those of Pfeiffer's salicylaldimine (*loc. cit.*) complexes. The sulphanilamide reacts with *o*-hydroxyaldehydes to form Schiff's bases, which function as bidentate chelate ligands. These complexes are insoluble in water, but are fairly soluble in different organic solvents. They may be regarded as true inner-metallic chelates. Their configuration may be represented as (I) :

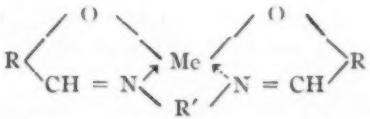


[I : R = C_6H_4, C_6H_3OH or $C_{10}H_6$; Me = bivalent metals or UO_2^{2+}].

The copper chelates of these ligands are all insoluble in water and are greenish-brown in colour. They show paramagnetic moment values of 1.72—1.96 μ_B, characteris-

tic of a planar configuration with hybrid dsp^2 bonds (Rây and Sen, this *Journal*, 1948, **25**, 473). The nickel, cobalt and manganese complexes all give moment values corresponding to their free ions. The formation of weak covalent bonds resonating with ionic ones are thereby suggested.

The metal chelates of resorcylaldehyde and β-hydroxynaphthaldehyde with *o*-phenylenediamine behave like the corresponding salicylaldehyde complexes described by Pfeiffer *et al.* (*loc. cit.*). The copper-resorcylaldehyde-*o*-phenylenediamine shows a magnetic moment value of 1.70 μ_B. The nickel-resorcylaldehyde-*o*-phenylenediamine, nickel-β-hydroxynaphthaldehyde-ethylenediamine and nickel-β-hydroxynaphthaldehyde-*o*-phenylenediamine have all been found to be diamagnetic and orange-red in colour. They are therefore penetration chelate complexes with square planar dsp^2 hybrid bonds (Rây, this *Journal*, 1948, **25**, 3). Cobalt-resorcylaldehyde-*o*-phenylenediamine gives an unusual moment value of 2.25 μ_B but the corresponding complex with β-hydroxynaphthaldehyde and *o*-phenylenediamine shows a moment value of 4.20 μ_B. The former possibly represents a penetration complex with square planar dsp^2 hybrid bonds with some contribution from the orbital moment. The latter, with a moment value more or less equal to that for a simple cobaltous ion, suggests the formation of planar weak sp^2d bonds resonating with ionic ones. The manganese compounds show moment values of 5.27-6.01. The configuration of these complexes are therefore either planar with sp^2d, or tetrahedral with sp^3, covalent bonds resonating with those of the ionic types. The configuration of these metal chelate compounds may be represented as shown below:



[where Me = bivalent metals ; R = $C_6H_3(OH)$ or $C_{10}H_6$ and R′ = C_2H_4 or C_6H_4]

EXPERIMENTAL

General Method of Preparation.—The metallic chelate complexes of bivalent copper, nickel, cobalt, manganese and of sexivalent uranium with different *o*-hydroxyaldehydes and *p*-aminophenylsulphonamide (sulphanilamide), *o*-phenylenediamine or ethylenediamine, were obtained as usual by the interaction of *o*-hydroxyaldehydes (2 mol.), amines (1-2 mol.) and the corresponding metal acetates (1 mol.) in hot aqueous ethanol mixture.

The compounds could also be prepared by the action of the different Schiff's bases, obtained by the condensation of the aldehydes and amines, with metal acetates in hot ethanol. The products obtained were usually purified by recrystallisation from hot alcohol.

General Properties

The compounds are generally insoluble in water, and soluble in ethanol and many organic solvents like alcohol, dioxan, pyridine, methoxyethanol, acetone, etc. They are fairly stable and are soluble in dilute alkalies, but are decomposed by mineral acids.

1. *Copper-salicylaldehyde-sulphanilamide* forms deep brown shining crystals [Found: Cu, 10.33; N, 9.15; S, 10.43; salicylaldehyde, 38.99. $Cu(C_{13}H_{11}O_3N_2S)_2$ requires Cu, 10.36; N, 9.13; S, 10.43; salicylaldehyde, 39.77 per cent].

2. *Nickel-salicylaldehyde-sulphanilamide* forms greenish-yellow crystals. [Found: Ni, 9.68; N, 9.23; S, 10.48; salicylaldehyde, 40.38. $Ni(C_{13}H_{11}O_3N_2S)_2$ requires Ni, 9.64; N, 9.20; S, 10.52; salicylaldehyde, 40.09 per cent].

3. *Cobalt-salicylaldehyde-sulphanilamide* forms reddish brown crystals [Found: Co, 9.68; N, 9.22; S, 10.50. $Co(C_{13}H_{11}O_3N_2S)_2$ requires Co, 9.68; N, 9.20; S, 10.52 per cent].

4. *Uranyl-salicylaldehyde sulphanilamide* forms orange-red crystals. [Found: U, 29.02; N, 6.85; S, 7.82. $UO_2(C_{13}H_{11}O_3N_2S)_2$ requires U, 29.02; N, 6.83; S, 7.82 per cent].

5. *Manganese-salicylaldehyde - sulphanilamide* forms shining brown crystals [Found: Mn, 9.11; N, 9.25; S, 10.54. $Mn(C_{13}H_{11}O_3N_2S)_2$ requires Mn, 9.08; N, 9.25; S, 10.58 per cent].

6. *Copper-resorcylaldehyde-sulphanilamide*: brown shining crystals. [Found: Cu, 9.86; N, 8.66; S, 9.92. $Cu(C_{13}H_{11}O_4N_2S)_2$ requires Cu, 9.85; N, 8.67; S, 9.91 per cent].

7. *Copper-β-hydroxynaphthaldehyde-sulphanilamide*: greenish brown crystals. [Found: Cu, 8.89; N, 7.85; S, 8.98. $Cu(C_{17}H_{13}O_3N_2S)_2$ requires Cu, 8.91; N, 7.85; S, 8.97 per cent].

8. *Copper-resorcylaldehyde-o-phenylenediamine*: shining-green crystals. [Found: Cu, 14.05; N, 6.04; H_2O (by loss at 108°), 11.68. $Cu(C_{20}H_{14}O_4N_2)$, 3 H_2O requires Cu, 13.71; N, 6.04; H_2O, 11.65 per cent]. [Found (dried at 108°): Cu, 15.62. Calc. Cu: 15.54 per cent].

9. *Nickel-resorcylaldehyde-o-phenylenediamine*: shining red needle-shaped crystals. [Found: Ni, 12.31; N, 5.78; H_2O (by loss at 110°), 15.08. $Ni(C_{20}H_{14}O_4N_2)$, 4 H_2O requires Ni, 12.31; N, 5.88; H_2O, 15.10 per cent]. [Found (dried at 110°): Ni, 14.52. Calc. Ni: 14.50 per cent].

10. *Cobalt-resorcylaldehyde-o-phenylenediamine*: brick-red crystals. [Found: Co, 13.66; N, 6.54; H_2O (by loss at 110°), 6.24. $Co(C_{20}H_{14}O_4N_2)$, 1.5 H_2O requires Co, 13.64; N, 6.48; H_2O, 6.25 per cent]. [Found (dried at 110°): Co, 14.51. Calc. Co: 14.56 per cent].

11. *Manganese-resorcylaldehyde-o-phenylenediamine*: reddish brown crystals. [Found: Mn, 13.44; N, 6.83. $Mn(C_{20}H_{14}O_4N_2)$, 0.5 H_2O requires Mn, 13.40; Co: N, 6.83 per cent].

12. *Nickel-β-hydroxynaphthaldehyde-ethylenediamine*: orange-red shining crystals. [Found: Ni, 12.24; N, 5.85; H_2O (by loss at 110°), 10.58. $Ni(C_{24}H_{18}O_2N_2)$, 3 H_2O requires Ni, 12.26; N, 5.84; H_2O, 11.28 per cent]. [Found (dried at 110°): Ni, 13.89. Calc. Ni: 13.82 per cent].

13. *Nickel-β-hydroxynaphthaldehyde-o-phenylenediamine*: orange-red shining crystals. [Found: Ni, 12.23; N, 5.82. $Ni(C_{28}H_{18}O_2N_2)$, 0.5 H_2O requires Ni, 12.19; N, 5.82 per cent].

14. *Cobalt-β-hydroxynaphthaldehyde-o-phenylenediamine* forms deep reddish brown crystals. From pyridine it recrystallises with pyridine of crystallisation. [Found : Co, 12.04 ; N, 5.75 ; H_2O (by loss at 110°), 3.68. Co ($C_{28}H_{18}O_2N_2$), H_2O requires Co, 12.01; N, 5.71 ; H_2O, 3.67 per cent]. [Found (dried at 110°) : Co, 12.48. Calc. Co, 12.47 per cent].

15. *Manganese-β-hydroxynaphthaldehyde-ethylenediamine* : brown crystals. [Found: Mn, 12.06 ; N, 6.11 ; H_2O (by loss at 108°), 7.43. Mn ($C_{24}H_{18}O_2N_2$), 2 H_2O requires Mn, 12.01 ; N, 6.10 ; H_2O, 7.87 per cent].

16. *Manganese-β-hydroxynaphthaldehyde-o-phenylenediamine* : brown crystals. [Found : Mn, 11.74 ; N, 5.98. Mn ($C_{28}H_{18}O_2N_2$) requires Mn, 11.71 ; N, 5.97 per-cent].

TABLE I

Magnetic measurements.

Compound No.	$\chi_g \times 10^6$	$\chi_m \times 10^6$ observed.	$\chi_m \times 10^6$ corrected.	Temp.	μ_B (effective).
1.	2.027	1245	1321	30°	1.80
2.	8.218	5003	5079	30°	3.52
3.	13.42	8171	8247	30°	4.49
4.	−0.2869	−235.4	...	30°	Diamagnetic
5.	24.30	14700	14775	30°	6.01
6	1.735	1121	1206	30°	1.72
7	2.017	1440	1576	30°	1.96
8.	2.337	1084	1183.9	30.5°	1.70
9.	−0.2385	−113.5	...	30 5°	Diamagnetic
10.	4.612	1992	2076.2	30 2°	2 25
11.	27.56	11295	11368.7	30.2°	5.27
12.	−0.3206	−153.5	...	30.5°	Diamagnetic
13	−0.3045	−110.2	...	30.3°	,,
14	14.55	7130	7214 5	30°	4.20
15.	25.69	11740	11813	30.4°	5.37
16.	25.01	11730	11834	30°	5.38

General Method of Preparation of Schiff's Bases

The Schiff's bases of *o*-hydroxyaldehydes with amines like sulphanilamide, *o*-phenylenediamine or ethylenediamine, were prepared as usual by the condensation of *o*-hydroxyaldehydes (1-2 mol.) and amines (1-2 mol.) in hot ethanol. The bases were generally recrystallised from hot alcohol.

17. *Resorcylaldehyde-sulphanilamide* : yellow shining crystals. [Found : C 53.68 ; H, 4.22 ; N, 9.61 ; S, 11.02. $(OH)_2C_6H_3CH = N.C_6H_4.SO_2NH_2$ requires C, 53.42 ; H, 4.11 ; N, 9.39 ; S. 10.96 per cent].

18. *β-Hydroxynaphthaldehyde-sulphanilamide* : orange-red shining crystals. [Found . C, 62.62 ; N, 8. 63 ; S, 9.82 ; (OH).$C_{10}H_6CH = NC_6H_4SO_2NH_2$ requires C, 62.58 ; N, 8.59 ; S, 9.82 per cent].

19. *β-Hydroxynaphthaldehyde-o-phenylenediamine* : yellow shining crystals. [Found : N, 6.75. (OH). $C_{10}H_6.CH = N.C_6H_4.N = CH.C_{10}H_6$(OH) requires N, 6.73 per cent].

20. *β-Hydroxynaphthaldehyde-ethylenediamine* : yellow shining crystals. [Found : N, 7.62. (OH). $C_{10}H_6.CH = N.CH_2.CH_2.N = CH.C_{10}H_6$ (OH) requires N, 7.60 per cent].

The Schiff's bases are all insoluble in water, but soluble in alcohol, pyridine, dioxan, etc.

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PLANT ALKALOIDS. PART VII. LAMBERTINE AND BERLAMBINE

By R. Chatterjee and P. C. Maiti

Chemical and physical evidence have been put forward to establish that structurally lambertine is dihydroanhydroberberine, and berlambine is indentical with oxyberberine. The presence of these two bases in association with berberine in nature and the production of oxyberberine and dihydroanhydroberberine from berberine by the action of alkali (Gadamer, *Arch. Pharm.*, 1910, **248**, 670) indicate that the bases are formed *in vivo* from berberine by processes of oxidation and reduction respectively.

In a previous communication (this *Journal*, 1953, **30**, 705) it was reported that two bases, which appeared to be hitherto unknown, had been isolated from *Berberis lambertii*, Parker and had been provisionally called lambertine and berlambine.

It has now been found that berlambine has one methylenedioxy group, two methoxyl groups and its molecular formula, $C_{20}H_{17}O_5N$, and its m.p. 199-200° are identical with those of oxyberberine, an oxidation product of berberine. Oxyberberine has been isolated so far from only one species of plant, *Berberis thunbergii*, DC. var. *maximowiczii*, Regel (Kondo and Tomita, *Arch. Pharm.*, 1930, **268**, 549). Berlambine is obtained as golden yellow needles from acetone and responds to the colour reaction of oxyberberine, which was obtained by Perkin as colorless plates from xylene (*J. Chem. Soc.*, 1890, **57**, 992). To compare berlambine with oxyberberine, the latter was prepared from berberine by the action of alkali (Gadamer, *Arch. Pharm.*, 1910, **248**, 670; Perkin, *J. Chem. Soc.*, 1918, **113**, 722). It is interesting to record that oxyberberine crystallises from acetone as yellow needles and from xylene as colorless plates. Berlambine crystallises, likewise, as colorless plates from xylene, and does not depress the m.p. of oxyberberine. Therefore, berlambine is identical with oxyberberine.

The other yellow base, lambertine, $C_{20}H_{19}O_4N$, also contains one methylenedioxy and two methoxyl groups. The nitrogen atom seems to be tertiary. It is reduced to a colorless crystalline base, $C_{20}H_{21}O_4N$, m.p. 172°, identical with tetrahydroanhydroberberine, m.p. 173°. Therefore, berlambine is almost certainly identical with dihydroanhydroberberine, m.p. 166-67°. The latter compound has been prepared according to Gadamer (*loc. cit.*) and also by reducing berberine with lithium aluminium hydride, and its properties compared with those of lambertine to establish the identity of lambertine with dihydroanhydroberberine. Although frequent occurrence of tetrahydroanhydroberberine with berberine has been reported in plants, dihydroanhydroberberine so far has not been known to be associated with berberine. The isolation of berlambine (oxyberberine) and lambertine (dihydroanhydroberberine) together with berberine from *B. lambertii* indicates that processes of oxidation and reduction respectively have taken place *in vivo*, yielding berlambine and lambertine from berberine.

Experimental

Berlambine.—A trace of the base was treated with a few drops of 50% H_2SO_4 and one drop of HNO_3 when the deep brown colour of the solution changed to intense violet. The m.p. 199-200° of berlambine was not depressed on admixture with a sample of oxyberberine, m.p. 199-200°. (Found: OMe, 17.7; CH_2O_2, 12.85. Calc. for $C_{20}H_{17}O_5N$: 2OMe, 17.66; one CH_2O_2, 13.1 per cent). The ultraviolet absorption spectra of berlambine and oxyberberine were identical. The principal absorption maxima and minima in ethanol were: $\lambda_{max.}$ 223.5 (log ϵ, 4.7198); 290 (4.0109); 340 (4.4651); $\lambda_{min.}$ 285 (log ϵ, 3.9070), 292.5 (3.9494).

Lambertine.—The base is sparingly soluble in methanol or acetone, from which it crystallises as yellow needles, m.p. 163°. It dissolves more readily in benzene or ethanol. (Found in a vacuum dried sample: OMe, 18.2; CH_2O_2, 13.41. $C_{20}H_{19}O_4N$ requires 2OMe, 18.4; CH_2O_2, 13.65 per cent). The ultraviolet absorption spectra of lambertine and dihydroanhydroberberine were identical. The principal absorption maxima and minima in ethanol were: $\lambda_{max.}$ 285 (log ϵ, 4.4580); $\lambda_{min.}$ 255 (log ϵ, 3.6381), 320 (3.2419).

Reduction of Lambertine with Zinc and Acetic Acid.—The base (0.1 g.) was reduced on a water-bath with zinc powder (1 g.) and glacial acetic acid (10 c.c.) and HCl (5 c.c.) till the deep yellow colour of the solution practically vanished. The solution was then filtered and treated with ammonia till the precipitated zinc hydroxide redissolved. The alkaline mixture was extracted with ether, on removal of which a colorless residue was left which could be crystallised from methanol, m.p. 172°. The crystals did not depress the m.p. of an authentic specimen of tetrahydroanhydroberberine, m.p. 173°, prepared by reducing berberine.

Action of Sodium Hydroxide on Berberinium Sulphate.—The method of conversion of berberinium sulphate into oxyberberine and dihydroanhydroberberine, as reported by Gadamer (*loc. cit.*, p. 676); was followed. Comparison of the properties of oxyberberine with those of berlambine establishes the identity of the two bases.

Synthetic dihydroanhydroberberine, m.p. 164-65°, did not depress the m.p. of lambertine, m.p. 163°, and both the bases showed identical ultraviolet absorption spectra (*loc. cit.*).

Reduction of Berberine with Lithium Aluminium Hydride.—A sample of dihydroanhydroberberine, obtained by the reduction of anhydrous berberine sulphate in dry ether with lithium aluminium hydride according to Schmid and Karrer (*Helv. Chim. Acta*, 1949, **32**, 960), had m.p. 166° and did not depress the m.p. of lambertine.

The variation in m.p. of *iso*quinoline bases in *Berberis* species is not without precedent. Kondo and Tomita (*Arch. Pharm.*, 1930, **268**, 553) reported that two fractions of oxyacanthine, obtained from the same source in the same experiment, melted at 217° and 209° respectively.

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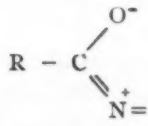
THE STRUCTURE OF AMIDES AND PARACHOR

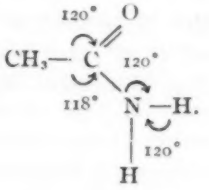
By R. P. Shukla and R. P. Bhatnagar

Attempt has been made to elucidate the structure of amides in the light of parachor values.

Amides are known to behave strangely. Pauling ('Nature of Chemical Bond', 1954, p. 127) has suggested



a highly polar resonance form for amides because of a rather large value of about 3.4 D for amide group moment. Recent infra-red (Randall, Fowler, Fuson and Bange, 'Infra Determination of Organic Structure", 1949, p. 10) and X-ray (Senti and Harker, *J Amer. Chem. Soc.*, 1940, **62**, 2008) data seem to point quite clearly to the existence of the amide group in the keto form ($R\text{-}CONH_2$), rather than in a tautomeric equilibrium with the enolic form. By considering this form Bates and Hobbs (*ibid.*, 1951, **73**, 2154) have shown that an expected moment of the amide group can easily be calculated, and thus, have shown amide as



Because of the above calculations and the lack of necessity to call on a highly polar resonance structure to explain the magnitude of the moment, it is of interest to see if other evidence can be found in the support of resonance. Hence, in the present work, parachor has been resorted to for elucidation of the structure of amides.

The parachor of CH_3CONH_2 has been determined in the fused state by Sugden (*J. Chem. Soc.*, 1924, 1177) and by Turner and Merry (*ibid.*, 1910, **97**, 2068). The value is 148.8. Ray (this *Journal*, 1935, **12** 406) has found the value 141.6 in very dilute aqueous solutions, but his results are unreliable since molar fractions of acetamide are very low. Bhagwat *et al.* (*ibid.*, 1944, **21**, 179) found the value as 134.0, but their value also is not constant and goes on decreasing with increase of temperature and dilution. The same thing is observed in case of urea. We have determined the parachor of acetamide, benzamide and urea in alcohol and water as solvents, and our results are shown below.

TABLE I

Acetamide in water.

Temp.	'x'.	d.	r.	P_m.	P_x
20.1°	0.1792	1.0497	54 12	65.52	128.0
30.1°	,,	1.0433	52.66	65.25	126 0
20 1°	0.2044	1 0551	53 68	67.94	128.92
30 0°	,,	1.0452	51.79	67.72	126 09
20.0°	0.2280	1.0531	52.48	69 92	129 91
30 0°	,,	1.0470	50.48	69.63	128.60
20.2°	0.2559	1 0561	51.38	72.24	130 51
30.0°	0.2818	1.0553	48.77	74,14	130.0

Acetamide in MeOH (P_{MeOH} = 88.53)

26.5°	0 1550	0 8494	27 88	97.91	149 91
27.3°	0 1685	0 8544	28.445	98.786	149.51
27.2°	0 1810	0.8594	28 635	99.359	148.13
27.2°	0.1928	0.8687	29 957	100.115	148 51

Urea in water (P_{water} = 52 3).

Temp.	'x.'	d.	r.	P_m	P_x
26.0°	0.0986	1.0708	72.04	60 06	130.09
30 0°	,,	1.0673	70 79	59.9)	129 90
30.0°	0.1253	1.0854	70.79	62 20	131 00
26 0°	1.1493	1 1012	71.39	64.06	130 81
35.0°	,,	1.0967	69.82	63 99	130.32
28 6°	0 1838	1.0993	75 457	67.75	136.46

Urea in methyl alcohol.

28.9°	0.1060	0.8570	26 806	93 971	139 81
27 8°	0.1008	0.8529	26.472	93.923	141.92
26.0°	0 1000	0.8540	25.958	93 367	110.81
26.9°	0.0927	0 8555	28 282	93 29	140.01

Benzamide in methyl alcohol.

26 7°	0.0596	0.8481	26.767	99.911	279 51
27.6°	0.0601	0.8489	26 613	99 911	279.82
27.7°	0.0612	0.8494	26 461	100.04	280 90
27.7°	0.0600	0.8489	26 687	100 03	280.07

N. B. 'x', 'd', 'r', P_m, and P_x have usual meaning.

Thus the observed parachor of acetamide, benzamide and urea is 149.5, 280.1 and 140.8 respectively, while the calculated values for the ketonic formulae correspond to 150.8, 280.9 and 142.9. Hence, there is no necessity of the highly polar resonance structures. In water as solvent the value is rather low which may be due to the ionisation caussing lowering (Bhagwat *et al.*, this *Journal*, 1944, **21**, 53; 1949, **26**, 39). The ionisation is also suggested by Wheland ("The Theory of Resonance", 1947, p. 181.).

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PREPARATION OF ANTIBACTERIALS FROM ORGANO-MERCURIALS. PART XII. A STUDY OF BIOCHEMICAL ANTAGONISM

By Sibanarayan Mahapatra, J. L. Ghosh and S. S. Guha Sircar

The antagonistic effect of some amino-acids, vitamins and organic sulphur compounds on the antibacterial activity of some organo-mercurials has been tested. A positive antagonism has been noted in each case.

Patnaik and Guha Sircar (this *Journal*, 1953, **30**, 577) reported the antagonism caused by a sulphur containing amino-acid, cystein, and by the vitamins, P. A.B. A. and nicotinic acid, when they were present in 1 : 5 molecular ratio, in solutions of some mercurated P. A. S. derivatives, which were inoculated with pure cultures of *E. coli* or *Staphylococcus aureus* (used as test organism). Rout and Guha Sircar (unpublished work) have also noticed the antagonism caused by the nicotinic acid and P. A. B. A. to the antibacterial action of many of the mercurated compounds, studied earlier by them (Parts V-XI of this series of investigations).

As such antagonism could not be explained by the well known Fildes-Woods theory of the metabolite competition, it was thought worth while to study systematically the antagonism, if any, that may be caused by a wide range of amino-acids, vitamins and organic sulphur compounds to the antibacterial action of some organic mercury compounds with a view to ascertaining the scope of application of (*a*) the metabolite competition theory of Woods and Fildes (*Brit. J. Expt. Path.*, 1940, **21**, 74 ; *Biochem. J.*, 1942, **36**, 3 ; *Lancet*, 1940, *i*, 955), (*b*) the antioxidant theory of Bernheim and Lehmann (vide *Svenska Lakartin*, 1946, **43**, 2029 ; *Rev. Gen. Sci.*, 1947, **54**, 222) in the case of P. A. S. and other benzoic acid derivatives, and (*c*) the metal-chelation theory of Fildes and Woods which sought to explain the antiseptic action of some organic mercurials, as being due to the -SH- combining capacity of these molecules (vide Porter, "Bacterial Chemistry and Physiology", p. 273, John Wiley, 1947).

The amino-acids, now chosen, are glycine, alanine, asparagine, and vitamin chosen is B_5 ; P. A. B. A. and sulphur compounds chosen are thioglycollic acid and thiosemicarbazides and their derivatives. The antibacterial compounds chosen are a few mercurated phenols and amines and a few mercurated aliphatic compounds, not studied earlier.

In Tables I and II, the analytical data of some of the compounds and their M. E. D. against the two organisms are summarised. Table III records the results of the study of the effect of the supposed antagonist to the action of four of the more active compounds, described in Tables I and II. It will be seen that the antagonism is positive in all cases. The effect caused by the sulphur compounds may be explained by the combination of the mercury atom with the -SH group ; the effect of the minute amounts of the amino-acids and the vitamin cannot at present be explained.

EXPERIMENTAL

The mercurated phenols, amines and aliphatic compounds were prepared by methods similar to those described by Newton Friend ("A Text-book of Inorganic Chemistry", Vol. XI, Part I").

TABLE I

[X denotes acetoxymercuri group].

No.	Compounds.	Decomp. point.	Colour.	% Mercury.		M. P. D.	
				Found.	Calc.	E. coli.	Stap. hur.
1.	X-5-methyl-resorcinol	210°	Light yellow	51.90	52.63	1 :1, 000	1 :70, 000
2.	Di-X-8-hydroxy-quinoline	< 250°	Deep red	61.10	60.60	Too sparingly soluble.	
3.	Di-X-4-chloro-resorcinol	200°	Light green	60 76	60.47	1 :60, 000	1 :120, 000
4.	*Nicotinic acid (Hg salt)	230°	White	43.65	44 80	1 :120, 000	1 :120, 000
5.	X-diphenylamine	210°	Light green	47.30	46.80	Too sparingly soluble.	
6.	X-4-aminoaceto-phenone	166°	Light yellow	50.00	50.90	Do	Do
7.	Hydroxymercuri-cinnamic acid	185°	White	54.25	54.95	1 :90, 000	1 :150, 000
8.	Hydroxymercuri-cyanoacetic acid	<250°	,,	67.20	66.60	1 :120, 000	1 :130, 000
9.	Hydroxymercuri-cyanoacetic ester	<250°	,,	59 98	60.68	1 :5, 000	1 :90, 000
10.	Di-X-maleic acid	210°	,,	63.60	63.19	1 :40, 000	1 :100, 000
11.	Di-X-phenol	215°	,,	64.80	65.60	1 :30, 000	1 :8, 000
12.	X-*p*-cresol	210°	,,	55.50	54 50	1 :50, 000	1 :4, 000
13.	X-thymol	140°	,,	49.25	49 02	1 :70, 000	1 :20, 000
14.	X-aniline	180°	,,	56.88	56.95	1 :50, 000	1 :20, 000

Most of the compounds described in Table I (except compounds No. 7, 8 & 9) contained the acetoxy mercuri group; acetic acid was set free on warming with 5% solution of KBr. The non-precipitation of yellow oxide of mercury on treatment with sodium hydroxide solution indicates that they are organo-mercury compounds and not the salts of mercury. Towards 1% cold solution of hydrazine sulphate, all these compounds were found to be stable, but most of them were gradually decomposed by H_2S on warming.

Except in case of compounds No. 7, 8 and 9 (Table I) one hundredth of a mole of the compound was dissolved in the minimum quantity of alcohol necessary to produce a clear solution (about 5 c. c. in each case) and one hundredth mole of the mercuric acetate, dissolved in the minimum quantity of dilute acetic acid, was added. These solutions were thoroughly mixed and kept overnight. The next day the precipitates were filtered off and washed with alcohol and then with water, and dried in the steam oven, and crystallised from hot dilute acetic acid. Cinnamic acid was dissolved in the minimum quantity of dilute caustic soda, to which one hundredth mole of yellow oxide of mercury was added, and the mixture heated on a water-bath for 4 to 6 hours. After cooling, the alkaline solution was acidified with dilute acetic acid,

and the precipitate was collected, washed with dilute alcohol and water and recrystallised from acetic acid. In the case of the mercuration of the cyanoacetic acid and cyanoacetic ester, one hundredth mole of yellow mercuric oxide was added and the mixture was shaken in an electric shaker for 48 hours, after which the mercurated derivatives appeared (Friend, *loc. cit.*, p. 51). The analysis of the mercury content was carried out by the usual gold crucible method.

The colour, melting point, mercury content of the compounds and the results of the biological tests, indicating maximum effective dilutions (M. E. D.) of the active compounds at 5 minutes' contact against *E. coli* and *Staphylococcus aureus* in broth medium at 37.5° using Rideal-Walker dilution method (observations being recorded after 24 hours) are recorded in Table I.

For the preparation of halogeno-mercuri derivatives, the solution of the compounds containing acetoxymercuri group in alcohol or acetic acid was added to water containing a slight excess of the alkali halide and the mixture was heated on a water-bath for two hours with occasional stirring. The precipitate formed was kept overnight, and filtered at the pump, washed with water repeatedly, and crystallised from acetic acid. The analytical results are shown in Table II.

TABLE II

Sr No	Compounds.	Decomp. Pt.	Colour.	% Mercury.		M. E.D.	
				Found.	Calc.	E. coli.	Staph. aur.
1.	Chloromercuri-2-aminopyridine	195°	Chocolate	57.85	58.75	1 :4, 000	1 :20, 000
2.	*p*-Bromomercuriphenol	200°	White	53.40	53.60	1 :30, 000	1 :8, 000
3.	2-Bromomercuri-*p*-cresol	210°	White	52.86	51.68	1 :8, 000	1 :1, 000
4.	Bromomercurithymol	190°	White	46.39	46.61	1 :4, 000	1 :1, 000
5.	*p*-Chloromercurianiline	186°	White	61.03	61.05	1 :30, 000	1 :4, 000
6.	Dichloromercuri-4-aminoacetophenone	...	Chocolate	65.80	66.02	1 :140, 000	1 :120, 000
7.*	Propylene oxide-mercuric dibromide	246°	White	57.10	56.60	1 :20, 000	1 :20, 000
8.*	Propyleneglycol-mercuric bromide	110°	White	55.99	56.30	1 :5, 000	1 :80, 000

* For preparation vide : "Text-book of Inorganic Chemistry" by Newton Friend, Vol. XI, Part I.

Table II shows that excepting compound No. 6, none of the products possess as high antibacterial activities as expected.

For testing the effects of the antagonists, the solutions of the mercury compounds were prepared in different molecular concentrations, spread over a range within which the drug was found to be active, in the preliminary experiments, the p_H of the solutions being adjusted between 6 and 8. The aqueous solutions of the amino-acids were separately prepared of the same molecular concentrations as the drugs. Equal volumes of the drugs and the antagonist solutions were mixed, inoculated with a 24-hour culture of the test organism, and after shaking and allowing to stand for 5 minutes, a loopful of the mixture was transferred to sterile nutrient broth in test tubes, and incubated. Observations were made after 24 hours' incubation. The results are summarised in Table III.

TABLE III

	Antagonists used.	Mercurated derivatives of nicotinic acid. M. E. D.		Mercurated derivatives of cinnamic acid. M. E. D.		Mercurated derivatives of cyanoacetic acid. M. E. D.		Dichloromercuri-4-aminoacetophenone. M. E. D.	
		E. coli.	Staph. aur.	E. coli.	Staph. aur.	E. coli.	Staph. aur.	E. coli.	Staph. aur.
1.	Without antagonist	1 :120, 000	1 :120, 000	1 :90, 000	1 :150, 000	1 :120, 000	1 :130, 000	1 :140 000	1 :120, 000
2.	Alanine	1 :10, 000	1 :20, 000	1 :40, 000	1 :20, 000	1 :20, 000	1 :60, 000	1 :10, 000	1 :40, 000
3.	Nicotinic acid	1 :40, 000	1 :40, 000	1 :20, 000	1 :20, 000	1 :20, 000	1 :10, 000	1 :10, 000	1 :40 000
4.	Tyrosin	1 :10, 000	1 :20, 000	1 :20, 000	1 :40, 000	1 :10, 000	1 :10, 000	1 :10, 000	1 :20, 000
5.	Asparagin	1 :10, 000	1 :20, 000	1 :20, 000	1 :40, 000	1 :10, 000	1 :10, 000	1 :10, 000	1 :10, 000
6.	Glycine	1 :20, 000	1 :20, 000	1 :20, 000	1 :40, 000	1 :20, 000	1 :20, 000	1 :10, 000	1 :60, 000
7.	Thioglycollic acid	1 :10, 000	1 :40, 000	1 :4, 000	1 :20, 000	1 :10, 000	1 :10, 000	1 :60, 000	1 :60, 000
8.	Cystein	1 :10, 000	1 :20, 000	1 :8, 000	1 :20, 000	1 :20, 000	1 :20, 000	1 :10, 000	1 :40, 000
9.	Thiosemicarbazide	1 :10, 000	1 :10, 000	1 :10, 000	1 :20, 000	1 :10, 000	1 :10, 000	1 :20, 000	1 :60, 000
10.	Methionine	1 :20, 000	1 :20, 000	1 :10, 000	1 :20, 000	1 :20, 000	1 :40, 000	1 :10, 000	1 :60, 000
11.	P. A. B. A.	1 :10, 000	1 :10, 000	1 :10, 000	1 :20, 000	1 :10, 000	1 :10, 000	1 :10, 000	1 :20, 000

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A NOTE ON THE PRODUCTION OF SILVER OXIDE IN THE DECOMPOSITION OF SILVER NITRITE

By T. M. Oza

The formation of silver oxide in the decomposition products of silver nitrite was closely searched for with negative results by Divers (*J. Chem. Soc.*, 1871, **24**, 85). Subsequently P. C. Ray and A. C. Ganguli (*Proc. Chem. Soc.*, 1905, **21**, 279), Oswald (*Compt. rend.*, 1911, **152**, 381), Checinski *et al.* (*Bull. Intern. acad. polonaise Classe Sci. Math. Nat.*, 1935-A, 155-65, 166-73) worked on the decomposition of silver nitrite, but reported no silver oxide among the products. The formation of silver oxide was, however, reported by K. M. Mehta (*Brit. Chem. Abs.*, 1942, Part-1, p.245) in the initial stage of the decomposition of silver nitrite. The details of the work have not been published as yet, but a perusal of it shows that the nitrate or the nitrite was heated in a current of air at 500°-550° when the residue showed alkaline reaction to phenolphthalein.

Formation of silver oxide in the decomposition of silver nitrite, if proved, would furnish a strong support to the primary stage in the decomposition of nitrites (Oza and Shah, *J. Univ. Bom.*, 1942, **11**, Part 3, p. 75) as

$$2\ MNO_2 \rightleftharpoons M_2O + NO + NO_2.$$

A careful study of the decomposition has shown that silver nitrite begins decomposing at about 128°. The rate at 130° is such that 0.35 g. does not all decompose in 12 hours, but at 230° half of it is decomposed in about 8 minutes. Only pure oxygen is left in the gaseous products of the decomposition at 480°. Evidence accruing from values of ratios of the solid products of the decomposition under different conditions shows the probability of rapid disappearance of a relatively unstable intermediate product, formed in the decomposition, leading to the production of silver.

Not a trace of nitrogen was ever found in the decomposition products.

Experiments with silver oxide showed that it reacted at 110° with nitric oxide to produce nitrate and nitrite ; with nitrogen dioxide it produced nitrate, nitrite and silver : all silver oxide did not react though excess nitrogen dioxide was present. Nitrogen dioxide reacted very slowly with silver nitrite at 120° and at higher temperatures it formed nitrate. The reaction of nitric oxide on silver nitrate was to bring the system to an equilibrium as

$$AgNO_3 + NO \rightleftharpoons AgNO_2 + NO_2$$

(Oza and Oza, *J. Chem. Soc.*, 1953, 907) as early as at 115°. This explains why nitrogen is not produced.

The above experiments show that the disappearance of silver oxide, if produced in the decomposition of silver nitrite, is due to its quick conversion to nitric oxide. To isolate silver oxide, the nitric oxide must be quickly destroyed.

By conducting experiments in an atmosphere of oxygen at 11 cm. pressure on the slow decomposition of silver nitrite at 130°, silver oxide has been isolated in the products in the experiments of duration of four hours and more. Addition of finely divided silver to silver nitrite did not increase the production of silver oxide but increased nitrate production slightly. Silver oxide is known to react with nitrogen dioxide to produce silver nitrate (Auden and Fowler, *Chem. News*, 1895, **72**, 163).

That silver oxide found in this way was not produced from silver and oxygen followed from the facts that (*i*) oxides of nitrogen were being continuously produced throughout from the slowly decomposing silver nitrite, and the finely divided silver was therefore not exposed to oxygen but to a mixture of nitrogen dioxide and oxygen ; (*ii*) not a trace of silver oxide had been isolated in experiments with pure silver nitrite between 140° and 240° when oxygen would be formed from nitrogen dioxide by dissociation (Richardson, *J. Chem. Soc.*, 1887, **51**, 397).

As quick decomposition of silver nitrite at 550° would leave silver in a finely divided state and the gases formed would be swept out of the system by the current of air, there is little doubt that the oxide reported in the thesis abstract, referred to, was formed from silver and oxygen : application of both affinity formula and free energy data shows that such a formation of silver oxide is possible. For details see Oza and Thacker (*J. Chem. Soc.*, 1925, 2457).

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SEARCH FOR NEW INSECTICIDES. PART X

By A. B. Sen and A. K. Sen Gupta

Xanthones containing nitro, amino, methoxy and alkyl groupings have been prepared with a view to testing them for their insecticidal activity.

Webster and Marshall (*J. Econ. Entomol.*, 1940, **33**, 909) experimented with nicotine and pyrethrin extracts, phenothiazine and commercial preparations containing xanthones, for coddling moth control, and observed that only xanthone preparations gave encouraging results. Insecticidal preparations containing bromo and methylated xanthones and a diluent were also patented by the General Chemical Company (B.P., 528, 752/1940). Xanthone-2 : 7-dinitrile was investigated by Fisher (*J. Amer. Chem. Soc.*, 1943, **65**, 991) for its insecticidal activity. Steiner and Summerland (*J. Econ. Entomol.*, 1943, **36**, 435) reported that xanthone was an effective ovicide against coddling moth, and Newcommer (*ibid.*, 1943, **36**, 344) found it potent against Pacific mites.

With a view to studying the effect of various substituents on the insecticidal acitivity, a number of alkyl-, methoxy- and amino-xanthones have been synthesised as these substituents are known to effect a marked variation in the solubility of the compounds in lipoid and water, an important factor controlling systemic action.

The substituted xanthones were obtained (*a*) by following the method of Ullmann (*Ber.*, 1904, **37**, 853) viz., through the condensation of the appropriate phenols with *o*-chlorobenzoic acids in methanol in the presence of copper powder and also (*b*) by the application of Nencki's reaction as applied by Seshadri and Pankajamani (*J. Sci. Ind. Res.*, 1954, **13A**, 396) for the preparation of xanthones.

Experimental

5-Nitro-2-chlorobenzoic acid was obtained by the nitration (HNO_3, *d* 1.5) of the 2-chlorobenzoic acid (Hubner, *Annalen*, 1884, **222**, 95), m.p. 165°. Reduction of the above with tin and hydrochloric acid (Hubner and Briedermann, *ibid.*, 1868, **147**, 264) furnished the amino acid, m.p. 158°.

5-Methoxy-2-bromobenzoic acid was obtained by the methylation of *m*-hydroxybenzoic acid, followed by the bromination with calculated amount of bromine (Graebe, *ibid.*, 1906, **340**, 211), m p. 150°.

4-Alkyl-2'-carboxydiphenyl Ethers.—The appropriate *o* chloro- or *o*-bromobenzoic acid was condensed with *p-tert.*-butylphenol, *p-tert.*-amylphenol and 6-*tert.*-butyl-*m*-cresol by the Ullmann method. (The alkyl phenols were obtained from Eastman Kodak Company, Rochester, N.Y.).

The alkylphenol (1 *M*) and the chlorobenzoic acid (1 *M*) were added to 20 c.c. of methanol, containing sodium (2 atoms) and a trace of copper powder and were refluxed for half an hour. The alcohol was evaporated to dryness and the dry brown substance was heated to 100°. The temperature of the bath was then raised to 140°; the contents

of the flask melted to a dark brown liquid at 120° (approx.) and solidified partly at 140°. When cooled, the contents were powdered and extracted with sodium carbonate solution, filtered and the filtrate acidified with dilute HCl, when the free acid separated out, which was recrystallised from the proper solvent.

The chlorobenzoic acids containing amino groups were first acetylated and then condensed with the respective phenols. The m.p. and N.E. of the acids, so obtained, are shown in Table I.

TABLE I

Name of the 2′-carboxy-diphenyl ethers.	M.P.	N.E.	Name of the 2′-carboxy-diphenyl ethers.	M.P.	N.E.
4-*tert.*-butyl-	130°	267	4-*tert.*-butyl-5′-amino-	150°	283
4-*tert.*-amyl-	135°	302	4-*tert.*-amyl-5′ amino-	149°	290
3 methyl-6-*tert* -butyl-	140°	280	3-methyl-6-*tert.*-butyl-5′-amino-	143°	289
4-*tert.*-butyl-5′-nitro-	129°	308	4-*tert.*-butyl-5′-methoxy-	140°	298
4 *tert.*-amyl-5′-nitro-	135°	422	4-*tert.*-amyl-5′-methoxy-	145°	310
3-methyl-6-*tert.*-butyl-5′-nitro	138°	423	3-methyl-5 *tert.*-butyl-5′-methoxy-	142°	311

The xanthones (Table II) were obtained from the above acids by the action of H_2SO_4 (conc., 10-12 c.c.) and heating on a water-bath for one hour. After cooling, the sulphuric acid solution was poured into water and the precipitate collected (excepting in the case of 3-methyl-4.*tert.*-butyl-5′- amino- acid where $POCl_3$ was used for ring-closure). The xanthones obtained were recrystallised from alcohol. The melting points, yields, percentages of carbon, hydrogen and nitrogen of the xanthones prepared are recorded in Table II.

TABLE II

Name of the xanthones.	M.P.	Yield.	%Carbon.		% Hydrogen.		% Nitrogen.	
			Found.	Calc.	Found.	Calc.	Found.	Calc.
2-*tert.*-butyl-	110°	77%	80.1	80.9	6.3	6.3	...	...
2-*tert.*-amyl-	125°	70	81.0	81.2	6.4	6.7	...	...
1-methyl-4-*tert.*-butyl-	115°	77	71.2	71.9	6.0	6.4	...	...
2-*tert.*-butyl 7-nitro-	140°	85	68.3	68.7	4.8	5.1	4.7	4.8
2-*tert.*-amyl-7-nitro-	130°	66	69.2	69.4	5.0	5.4	4.4	4.5
1-methyl-4-*tert.*-butyl-7-nitro-	155°	84	68.9	69.4	5.1	5.4	4.3	4.5
2-*tert.*-butyl-7-amino-	170°	55	75.9	76.4	6.2	6.3	5.1	5.3
2-*tert.*-amyl-7-amino-	173°	55	76.4	76.8	6.5	6.9	4.7	5.0
1-methyl-4-*tert.*-butyl-7-amino-	185°	63	76.6	76.8	6.4	6.9	4.9	5.0
2-*tert.*-butyl-7-methoxy-	180°	60	76.9	77.1	6.1	6.4	...	...
2-*tert* -amyl-7-methoxy-	156°	55	76.9	77.0	6.3	6.7	...	...
1-methyl-4-*tert.*-butyl-7-methoxy-	169°	54	76.7	77.0	6.4	6.7	...	...

Xanthones (Table III) were obtained by the usual Nencki's reaction (*loc. cit.*). Alkylsalicylic acids required in the above reaction were obtained from *p*-*tert.*-butyl- and *p*-*tert*-amylphenols by adopting the Reimer-Tiemann reaction (*Ber.*, 1876, **9**, 1288; Friedländer, Vol. XI, p. 210).

p-tert.-Butylphenol (15 g.) was dissolved in concentrated aqueous solution of KOH (33.6 g. in 84 c.c. of water) and warmed on a water-bath. CCl_4 (10 c.c.) and a small amount of freshly precipitated copper were then added to it and the mixture refluxed on a water-bath for ten hours; the unchanged CCl_4 was steam-distilled. The residue was then diluted with water, filtered and the filtrate acidified with HCl. The crude product was extracted with ether and the ethereal layer shaken with 10% sodium carbonate solution to separate the acid from the unchanged phenol. This alkylsalicylic acid was isolated by treating with dilute HCl and recrystallised from hot water. 2-Oxy-5-*tert.*-amylbenzoic acid was obtained in the similar manner. The melting point, yield and the neutralisation equivalent of the two acids are shown below.

	M.P.	Yield.	N.E.	
			Found.	Calc.
2-Oxy-5-*tert.*-butylbenzoic acid	152°	64 %	191.2	194.1
,, ,, amyl ,, ,,	132°	58	205.3	208.1

These alkylsalicylic acids were then condensed with *p-tert.*-butyl-, *p-tert*-amyl- and 6-*tert*-butyl-3-methylphenols by the following method.

A mixture of alkylsalicylic acid (1 *M*), alkylphenol (1 *M*) and freshly fused zinc chloride (10 g.) was heated to 200° slowly for five minutes; the temperature was then brought down to 180° and maintained for 4 hours. After cooling, the product was repeatedly washed with water to remove the unchanged components, and the residue was then taken up in ether and the ethereal extract dried over anhydrous sodium sulphate. The ether was removed by distillation and the residue crystallised from alcohol. The melting points, yields and the percentages of carbon and hydrogen are recorded in Table III.

TABLE III

Name of the xanthones.	M.P.	Yield.	% Carbon.		% Hydrogen.	
			Found	Calc.	Found.	Calc.
2 :7-Di-*tert.*-butyl-	182°	55 %	81.0	81.8	7.3	7.7
2-*tert.*-Butyl-7-*tert.*-amyl-	175°	54	81.1	81.9	8.0	8.1
1-Methyl-4 :7-di-*tert.*-butyl-	187°	56	81.0	81.9	7.9	8.1
2-*tert.*-Amyl-7 *tert.*-butyl-	190°	60	81.2	81.9	8.0	8.1
2 :7-Di-*tert.*-amyl-	192°	63	81.9	82.1	8.0	8.3
1-Methyl-4-*tert.*-butyl-7-*tert.*-amyl-	200°	65	81.8	82.1	7.9	8.3

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY,
LUCKNOW.

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OBITUARY

Dr. Rasik Lal Datta, D.Sc.

Rasik Lal Datta was a brilliant student of his time. He stood first both in the B.Sc. examination with Honours in Chemistry in 1910 and M.Sc. in Chemistry in 1912 from the Presidency College Calcutta. He was the recipient of several gold medals and prizes during his career as a student. He earned the distinction of securing Hemchandra Gossain gold medal and prize in 1912 by scoring highest marks in all the science subjects. He was awarded the Palit Research Scholarship in 1913 and D.Sc. degree in 1916. In the same year he obtained Premchand Raichand Scholarship and Griffith Memorial prize. In recognition of the merit of his post-graduate researches he was awarded research grants from the State Department, Washington; Chemical Society, London ; Royal Society, Great Britain ; Van't Hoff Memorial Fund and from the National Academy of Sciences, U.S.A. (1917-21).

Born: July 31, 1890.
Died: Aug. 4, 1955.

In 1915 he was appointed a demonstrator of chemistry in the Presidency College. In 1917 he joined the newly created University College of Science and Technology as an Assistant Professor of Chemistry and remained there till the later part of December, 1921. By the end of 1921 he was appointed Industrial Chemist of the Govt. of Bengal, which appointment he held till his retirement from service in 1945.

Rasik Lal owed his inspiration and initiation in Chemical research to Late Acharya Prafulla Chandra Ray. While he was a student of the fifth year class in chemistry in the Presidency College, discriminating eyes of Acharya Ray singled out Rasik Lal to collaborate with him in his researches on alkylammonium nitrites. Soon after, Sir P. C. Ray had the satisfaction of finding his choice amply justified. Within a short time of his research career under Sir P. C. Ray, he marked out for himself an independent line of enquiry on halogenation of organic compounds, and gradually in collaboration with his students published twenty three papers on the subject, some of which have found place in standard text-books of organic chemistry.

During 1911-1927 he published in collaboration with others no less than 56 papers on halogenation, formation of double salts, alkylammonium salts and allied lines in various chemical journals of Europe, America and India.

Since his appointment in the Department of Industries, Govt. of Bengal, in 1921, he directed his talent towards the solution of technical problems of chemical industries. His contribution in this sphere is no less brilliant than his academic researches in pure chemistry. His valuable contributions on soap-making have earned universal approbation of the soap technologists. His technical contributions in various journals, as Departmental bulletins and as Indian, British and American Patents occupy a considerable volume and number no less than eighty seven.

He was a member and first Chairman of the Oil and Soap Committee of the Industrial Research Bureau of Govt. of India (1933), Secretary, Bengal Industrial Research Board (1939), a Member of the Chemical Industries Sub-committee of the National Planning Committee (1939) and Salt Sub-committee of the Bengal Industrial Survey Committee (1940-41).

The brilliant achievements of Dr R. L. Datta in the field of Chemistry can be summed up in the words of Sir P. C. Ray as: "I am not aware of any other Indian who has given such marked proof of originality in the field of organic chemistry. The work of Rasik Lal Datta makes a record in the history of chemical science in India".

Dr. Rasik Lal Datta was intimately connected with the Indian Chemical Society. He was one of the four members constituting the sub-committe appointed by the Indian Science Congress for the founding of the Society. He was a Foundation Fellow and served on the Council of the Society as a Member for several terms. His tragic end is a great loss to the Society and to the chemical researches in India.

May his soul rest in peace!

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THERMAL DECOMPOSITION OF CALCIUM NITRITE. PART II

By Trambaklal Mohanlal Oza and Vasantrai Trambaklal Oza

Experiments are devised to demonstrate (*i*) the true form of equation representing the primary stage : no nitrite is formed in the interaction of calcium oxide with mixtures of nitrogen dioxide and nitric oxide and (*ii*) that nitrate is not formed in the primary stage under the conditions of the thermal decomposition. Nitrogen dioxide, in a mixture of the gas with nitric oxide reacts preferentially with calcium oxide to form nitrate.

The thermal decomposition of calcium nitrite was studied by P. C. Ray (*J. Chem. Soc.*, 1905, **87**, 177) and by Oza and Oza (*ibid.*, 1953, 907). The latter workers represented the reactions as follows :

I. The primary stage (cf. Ostwald, *Annalen*, 1914, **403**, 32) as

$$Ca(NO_2)_2 \rightleftharpoons CaO + NO + NO_2 \quad \ldots \quad \ldots \quad (1)$$

II. The action of nitrogen dioxide, produced in (1), on the undecomposed nitrite forming nitrate and nitric oxide as

$$Ca(NO_2)_2 + 2NO_2 \longrightarrow Ca(NO_3)_2 + 2NO \quad \ldots \quad \ldots \quad (2a)$$

and on calcium oxide as

$$2CaO + 4NO_2 \longrightarrow Ca(NO_3)_2 + Ca(NO_2)_2 \quad \ldots \quad (3)$$

III. The action of nitric oxide on calcium nitrite as

$$Ca(NO_2)_2 + 2NO \longrightarrow Ca(NO_3)_2 + N_2 \quad \ldots \quad \ldots \quad (4)$$

Nitric oxide formed in (1) and (2a) set (2a) backwards making the reaction reversible as

$$Ca(NO_2)_2 + 2NO_2 \rightleftharpoons Ca(NO_3)_2 + 2NO \quad \ldots \quad \ldots \quad (2)$$

and the occurrence of (2) abated (4).

The tendency of the decomposition to come to a standstill at a limiting stage was ascribed to reaction (3) regenerating nitrite. This reaction, which is characteristic of wet systems, is not likely to occur in the dry systems (Oza and Patel, this *Journal*, 1954, **31**, 519; Addison and Lewis, *J. Chem. Soc.*, 1953, 1874). Regeneration of nitrite may occur therefore only as in (2) when conditions permit.

Investigations on the interaction of nitric oxide with metal oxides by Oza and co-workers seemed to show that the mode of representing the primary stage as in (1) was incorrect as it implied formation of nitrite by the action of mixtures of nitrogen dioxide

and nitric oxide on metal oxide. Again, formation of nitrate was ascribed to primary stage by Ray, while Rendall, Manov and Brown (*J. Amer. Chem. Soc.*, 1938, **60**, 694) made the equation,

$$2AgNO_2(s) = AgNO_3(s) + Ag(s) + NO(g),$$

the basis for computing heat capacities of the involved substances. Oza, Oza and Thaker (*J. Chem. Soc.*, 1955, 2457) have shown that formation of silver nitrate does not occur in the primary stage. Oza and Walawalker (this *Journal*, 1945, **22**, 263) showed that nitrate-forming reaction occurred in the molten mass, while Oza and Oza (*loc. cit.*) showed that it occurred also at the solid (or melt)-gas interface. Inside the melt the reaction was mainly (2a), while at the interface it was mainly (4).

In the present work experiments are described to study (*i*) the system comprising CaO and mixtures of nitric oxide with less than its equivalent nitrogen dioxide at low temperatures; (*ii*) the slow decomposition of calcium nitrite at 360°, for varying periods of time, under continuous vacuum to reduce the extent of the interface reaction (4); (*iii*) the quick decomposition, at 500°, (*a*) in vacuo and (*b*) in oxygen atmosphere: (*b*) would facilitate reaction (3); and (*iv*) the moderate decomposition, at 410°-420°, (*a*) when the products of the reaction are allowed to stay in the system and (*b*) when (1) charcoal and (2) calcium oxide are added to calcium nitrite prior to decomposing the latter.

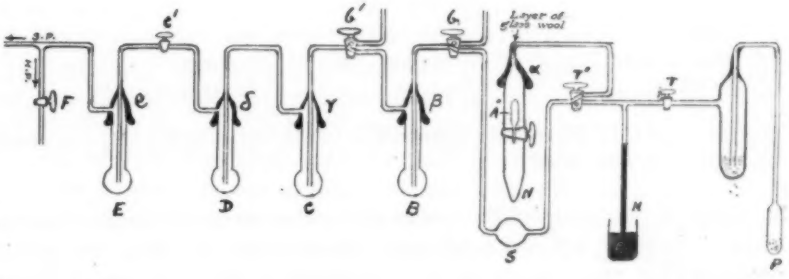
Experimental

Calcium nitrite was the same as that used by Oza and Oza (*loc. cit.*). Calcium oxide was the pure B.D.H. chemical heated to dull red heat in a platinum crucible and preserved in a desiccator: 0.0201 g. substance gave 0.0492 g. $CaSO_4$ (Found: Ca 71.86%. Calc. for CaO: Ca, 71.45%). Charcoal was extra pure (Oza, this *Journal*, 1944, **27**, 71). Analyses of the residue and the gas were carried out as by Oza and Oza (*loc. cit.*). In the experiment with charcoal the residue was repeatedly shaken with boiled out distilled water (cold) till the dissolved portion showed no alkalinity and no reaction for nitrite; this solution was worked up for oxide, nitrite and nitrate, and the insoluble portion was examined for calcium carbonate. The oxide was titrated immediately after dissolution. The alkali solution used in the apparatus to absorb nitrous fumes and carbon dioxide was examined for carbonate, nitrite and nitrate. The pumped gas contained very little (0.2 c.c.) carbon dioxide in addition to nitric oxide, carbon monoxide, nitrous oxide and nitrogen, and was analysed after removing carbon dioxide as follows: the absorbents (sodium sulphite and cuprous chloride) were saturated with nitrous oxide, the saturation point being tested. Nitric oxide was absorbed first and then carbon monoxide. Finally, the gas was passed through cold alcohol, renewed till no contraction. The residual gas was taken as nitrogen.

The apparatus used was the same as previously used by Oza and Oza (*loc. cit.*). For studying the action of mixtures of nitric oxide and nitrogen dioxide on calcium oxide, the apparatus shown in Fig. 1 was used.

S.P. denotes Sprengel pump and H. P., the Hyvac pump. A heavy tap is connected to a limb of T' through the ground glass joint, x; S is a bulb of 500 c.c. capacity; T', b and b are 3-way taps and the rest, c' etc., are 2-way taps. Q,B,C,D,E are connections through internal seals of which B,C,D,E contain ground glass joints. To begin with, sufficient silver nitrite is placed in P and the latter sealed on to the internal seal, Q, which contains a fairly saturated solution of KOH. The tube Å containing dinitrogen tetroxide (mass, roughly 0.04 to 0.07 g.) is arranged in 'N', as shown in the figure, with its capillary elongation passing through the bore of key of the tap. The system is then evacuated till 15 minutes after the characteristic click. The tap 'b' is then turned off to isolate its right from its left and the tap T' turned to connect 'S' with 'P'. Silver nitrite is then heated in a bath at about 140° to generate nitric oxide and the nitrous fumes, the latter being absorbed out in Q. Nitric oxide is allowed to collect till its pressure, as indicated by the manometer, M, is about 20 cm. (volume about 135-140 c.c. at N.T.P.). The tap 'T' is then turned off. 'b' is now turned to admit air into 'B' and P_2O_5 placed in 'B', and the portion of the system is then evacuated. b' is now turned off and 'b' opened to 'S' and nitric oxide allowed to be dried in contact with P_2O_5 for 2 hours; 'b' is now turned off, b' opened and the pump worked to remove the gas in the system to the left of 'b'. Air is then introduced into the system to the left of 'b', the portion B of the apparatus cleansed and dried, and a weighed quantity of calcium oxide is placed therein and the system fitted up with a layer of warm vacuum grease; the portion of the apparatus is evacuated and b' turned off so as to keep the system to its right in tact. Air is now introduced at 'F' into the system to the left of b' and a fairly saturated KOH solution is placed in C, D, E, and the system finally fitted up and completely evacuated.

FIG. 1



To start an experiment, T' is turned to connect 'Å' with 'S' and the key of the tap carefully turned to break the capillary of the nitrogen tetroxide tube, Å. The nitrogen tetroxide, so released, is allowed to get uniformly mixed up with nitric oxide in the bulb 'S' between 'b' and 'N': a homogeneous mixture is allowed to be formed by waiting for one hour. 'B' is then surrounded by a bath at the temperature of the experiment for about one hour and the Sprengel pump started. 'b' is now partially opened and so also b' and c' so that a slow stream of the gas mixture is bubbled through C, D and E after passing over

calcium oxide at 'B': this is continued for periods shown in Table I. The rate was so adjusted that during the time most of the gas was drawn off. At the end of the period, Hyvac pump was started to quickly remove the remaining gas out of the system. The results recorded in Table I show that although temperatures are maintained low, no appreciable nitrite is formed, only nitrate being produced in the interaction. The experiments therefore show conclusively that no nitrite is produced in the interaction between calcium oxide and the nitrous gases.

TABLE I

Action of a mixture of nitric oxide and nitrogen dioxide on calcium oxide at and below 0°.

Volume of nitric oxide in the system = 135-140 c.c. (N T.P.).

Expt. No.	Temp.	Duration of expt.	N_2O_4 taken (g.).	CaO taken.	Products formed. $Ca(NO_3)_2$.	Products formed. $Ca(NO_2)_2$.	N_2O_3 * absorbed (c.c.).
1	0.2° Melting ice	½ hr.	0.0482 (11.74 c.c.)	0.1010 g.	0.00112 g. (0.07×10^{-4})	Not a trace	23.2
2	Do	2	0.0654 (15.92 c.c.)	0.1001	0.01330 (0.8×10^{-4})	Trace only	28.8
3	Intimate freezing mixture of ice & common salt	1	0.0510 (12.43 c.c.)	0.1002	0.0048 (0.29×10^{-4})	Do	22.66
4	Intimate freezing mixture of $FeCl_3$+ice	2	0.0716 (17.45 c.c.)	0.1000	0.0136 (0.83×10^{-4})	Do	30.2

* Unreacted at end of the reaction, calculated as $2KOH + N_2O_3 = 2KNO_2 + H_2O$ (no nitrate formed in presence of the alkali).

In Table II are recorded the results of experiments on the thermal decomposition of calcium nitrite under different conditions. Experiments 1-4 show the results when the decomposition runs slowly at 360°, respectively for 1,2,3 and 4 hours. The gaseous products of the decomposition are pumped off, as formed, by working the Sprengel pump continuously. The results show that there is very little nitrogen in the gas, and the production of nitrate steadily diminishes with increasing time though increasing amounts of nitrite are used up, but the production of oxide increases (ratio column).

These experiments show that nitrate is not formed in the primary stage and that at least a part of it is formed by the action of the gases on calcium oxide ; for, when such action is not allowed to occur, oxide accumulates and production of nitrate suffers.

TABLE II

Expt. No.	Time.	Mass of $Ca(NO_2)_2,H_2O$.	Residue (in g.). Nitrite.	Nitrate.	Oxide.	Gas evolved (N.T.P.) (in c.c.). NO.	NO_2.	N_2.	$Ca(NO_2)_2$ used up.
			Temp. = 360°						
1	1 hr.	0.2510 (0.2210)*	0.2106	0.0039 (0.24×10^{-4})†	0.0031 (0.55×10^{-4})†	2.0	0.5	...	0.0104 g. (0.78×10^{-4})†
2	2	0.2508 (0.2206)	0.2035	0.0046 (0.28×10^{-4})	0.0054 (0.97×10^{-4})	3.8	0.6	Bubble	0.0171 (1.3×10^{-4})
3	3	0.2502 (0.2204)	0.1966	0.0052 (0.32×10^{-4})	0.0080 (1.45×10^{-4})	5.8	0.8	0.1	0.0238 (1.8×10^{-4})
4	4	0.2515 (0.2215)	0.1884	0.0060 (0.36×10^{-4})	0.0105 (1.9×10^{-4})	7.5	1.1	0.15	0.0331 (2.5×10^{-4})
			Temp. = 500°						
5	10 min.	0.2498 (0.2199)	0.1020	0.0587 (3.58×10^{-4})	0.0300 (5.5×10^{-4})	20.0	0.6	1.6	0.1179 (8.9×10^{-4})
6	,,	0.2546 (0.2241)	0.1060	0.0579 (4.1×10^{-4})	0.0275 (4.9×10^{-4})		21.5	Trace	0.1181 (8.9×10^{-4})
7	,,	0.2500 (0.2200)	0.0980	0.0501 (3.1×10^{-4})	0.0354 (6.3×10^{-4})	..	...	...	0.1220 (9.2×10^{-4})

* Figures in parentheses show corresponding mass of anhydrous nitrite.

† The quantities in g. mols.

Experiments 5, 6 and 7 show the results of quicker decomposition at 500° in 10 minutes respectively, when (*a*) the gases are allowed to stay in the system (expt. 5), (*b*) when the decomposition proceeds in an atmosphere of oxygen so that nitric oxide can become nitrogen dioxide (expt. 6) and (*c*) when the decomposition occurs under the continuous vacuum of the Hyvac pump (expt. 7). The apparatus used in studying the decomposition in the atmosphere of oxygen was the same as used by Oza and Oza (*loc. cit.*) with a T-containing potassium chlorate tube under a stop-cock to produce oxygen. Expt. 5 shows normal results and the expts. 6 and 7 show the effect of the imposed conditions (by comparison): in expts. 5 and 6 the amount of nitrite decomposed is the same and yet less oxide and more nitrate are formed in expt. 6 than in expt. 5, showing that nitrogen dioxide produces nitrate from the oxide. This conclusion is also supported by the results of expt. 7 in which a little more nitrite is consumed than in expts. 5 and 6, and yet less nitrate is produced while oxide produced is more.

Table III shows the results of experiments at 420° for one hour. Expt. 8 shows the results when 20% (on the mass of nitrite) pure charcoal is intimately mixed, by grinding together, with the nitrite, and the mixture allowed to decompose. Expt. 9 shows the results when 20% calcium oxide is so mixed. In expt. 8 the reaction commenced, though very slowly, at 260° but became quite appreciable at 388°–390°, and developed great speed as temperature rose; the residue contained very little nitrite and no nitrate at all: it contained carbonate, oxide and hyponitrite while the gas showed the presence of some nitrous oxide and carbon monoxide in addition to nitrous gases and nitrogen. The presence of nitrous oxide is due to hyponitrite whose presence

in the residue has been confirmed after Oza (*loc. cit.*, p. 72). Experiment 9 also showed greater speed as compared with the speed when nitrite alone decomposed. Calcium oxide, being a product of the dissociation, may be expected to retard the reaction, but in the present case nitrogen dioxide, another product of the dissociation, reacts with it and the reaction is more complete when its amount is (as now) greater than when it was less as when produced in the decomposition alone ; the relative amount of nitrate is greater in this experiment.

TABLE III

Action of charcoal and CaO *on the decomposition of calcium nitrite.*

Temp. = 420°. Time = 1 hr.

Mass in g.		Residue			$Ca(NO_2)_2$ consumed.	Gas formed (N.T.P.) in c.c.					
$Ca(NO_2)_2.H_2O$.	C or CaO.	$Ca(NO_2)_2$.	$Ca(NO_3)_2$.	$CaCO_3$. CaO.		Total.	CO_2.	NO.	N_2O.	CO.	N_2.	NO_2.
				Expt. 8.								
0.2074 (0.1757)*	C : 0.0491	0 0157	Nil	0.0701 0.0285 (7.0×10^{-4}) (5.1×10^{-4})	0.1600 (12.1×10^{-4})†	36.1	0.2	19.3	4.0	1.2	11.3	0 3
				Expt. 9.								
0.2000 (0.1755)	CaO : 0.0500	0.0913	0.0343 (2.1×10^{-4})	Total CaO : 0 0742	0.0847 (6.4×10^{-4})	17.7	...	16.5	...	...	0.4	0.8
				CaO formed : 0.0242 (4.3×10^{-4})								

* Figures in parentheses show mass of analysed nitrite.

† ,, ,, are in g. mols.

CONCLUSION

The primary stage in the decomposition of nitrites consists of dissociation of the nitrite into oxide and nitrogen trioxide, the latter then decomposing into nitric oxide and nitrogen dioxide, and may be reprsented as

$$2MNO_2 \rightleftharpoons M_2O + N_2O_3 (= NO + NO_2).$$

Nitrate does not seem to be produced in the primary stage. In its formation by the interaction of oxides with nitrous gases, comprising mixtures of nitrogen dioxide, nitric oxide and oxygen (produced by dissociation of nitrogen dioxide), the involved reaction, (Oza and Patel, this *Journal*, 1954, **31**, 522) which brings about formation of nitrate, may be

$$M_2O + 2NO_2 + O = 2MNO_3.$$

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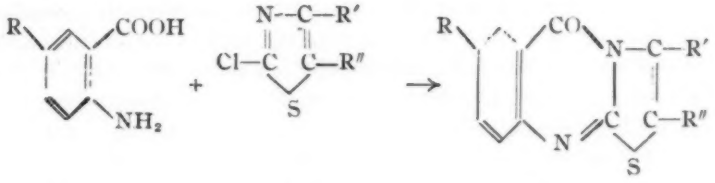
THIOPEGAN DERIVATIVES. PART VII

By H. S. Sachdev and K. S. Narang

Several 10 : 11-thiopegan derivatives have been synthesised with a view to testing their therapeutic activities. Structure of one of the two compounds, obtained by the condensation of 2-carbethoxy-4-methylphenylthiourea with monochloroacetone, has been established.

Preparation of 2-chlorothiazoles (II) (unpublished) has made it possible to utilise the same for an unambiguous synthesis of 10 : 11-thiopegan derivatives (III) (Table I) by the following route.

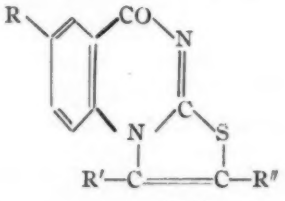


(I) (II) (III)

[R = H or Me; R′, R″ = various groups]

The condensation of (I) with (II) was effected as detailed in the experimental part. Attempted condensation of (I: R = H) with (II: R′ = Ph ; R″ = H) by refluxing in ethanol solution for 12 hours did not materialise. Condensation of (I) with the hydrochloride of (II : R′ = *p*-methoxyphenyl ; R″ = H) or condensations of (II: R′ = phenyl ; R″ = H) with ethyl ester of (I : R = H) or its hydrochloride did not affect the yields. The yields did not improve either by the condensation of (I: R = H) with (II: R′ = Ph ; R″ = H) in phenol melt or in presence of Cu powder or NaI.

The compound No. 5 (Table I) has been found to be identical with one of the two isomeric products (m.p. 180-81°) obtained by the condensation of 2-carbethoxy-4-methylphenylthiourea with monochloroacetone (Dhatt and Narang, Part III, *J. Org. Chem.*, 1955, **20**, 302). The higher melting isomer with m.p. 307-308° therefore would have the angular structure (IV: R = Me; R′ = Me; R″ = H).



(IV)

It is also to be mentioned that the various compounds in Table I have lower melting points than their corresponding isomers obtained by the condensation of 2-carbethoxyphenylthiourea or its 4-methyl derivative with various haloketones

in Part I (Narang *et al. J. Sci. Ind. Res.*, 1953, **12B**, 469) and in Part III (*loc.cit.*). The compounds in Parts I and III, referred to above, may possess the angular structures of the general type (IV). This requires further confirmation through unambiguous synthesis.

Experimental

10:11-*Thiopegan Derivatives* (III).—The reaction between 2-chloro-4-(*p*-chlorophenyl)-thiazole and anthranilic acid is a typical case of the series. A mixture of the chlorothiazole (2 g.) and anthranilic acid (1.19 g.) was heated in an oil-bath with occasional stirring. At 110°-130° the mixture became mobile, and brisk reaction started at 165°. It was heated at 180° for 1½ hours when the molten reaction mixture became a semisolid. During the reaction a small amount of a white sublimate, probably that of the acid hydrochloride, condensed on the sides of the tube. It was occasionally scratched and mixed with the main mass. After allowing it to cool, ethanol (10 c.c.) was added and the mixture was warmed. It was made alkaline with sodium bicarbonate and the light grey solid (1.75 g., m.p. 130-40°) was collected on suction, washed with water to free it from bicarbonate and crystallised from 95% ethanol in colorless needles, m.p. 235-36°, the yield being 0.5 g. All the products were crystallised from dilute ethanol.

Table I

Formation of 10:11-*thiopegan derivatives* (III: $R'' = H$).

No.	2-Chlorothiazoles.	Product. R.	R'.	Yield.	M.P.	Mol. formula.	Found.	Calc
			With anthranilic acid.					
1	-4-(phenyl)-	H	Ph	14.0%	214-15°	$C_{16}H_{10}N_2OS$	S : 11.88	11.51%
2	-4-(*p*-chlorophenyl)-	H	C_6H_4Cl (*p*)	12 9	235-36°	$C_{16}H_9N_2OClS$	N : 8.85	8.96
3	-4-(*p*-bromophenyl)-	H	C_6H_4Br (*p*)	9.3	239-40°	$C_{16}H_9N_2OBrS$	N : 8.08	7.84
4	-4-(*p*-tolyl)-	H	$C_6H_4CH_3$(*p*)	15 9	195-96°	$C_{17}H_{12}N_2OS$	N : 9 38	9.59
			With 5-methylanthranilic acid.					
*5	-4-methyl-	Me	Me	54.5	180-81°	$C_{12}H_{10}N_2OS$	N :12.20	12.17
6	-4-phenyl-	,,	Ph	14 3	197-98°	$C_{17}H_{12}N_2OS$	N : 9 91	9.59
7	-4-(*p*-chlorophenyl)-	,,	C_6H_4Cl (*p*)	24.6	219°	$C_{17}H_{11}N_2OClS$	N : 8.48	8.59
8	-4-(*p*-bromophenyl)-	,,	C_6H_4Br (*p*)	26.5	228-29° (d) shrinks at 215°.	$C_{17}H_{11}N_2OBrS$	N : 7.40	7.54
9	-4-(*p*-tolyl)-	,,	$C_6H_4CH_3$(*p*)	24 0	194-95°	$C_{18}H_{14}N_2OS$	N :8.80	9.15
10	-4-(*p*-methoxyphenyl)-	,,	$C_6H_4OCH_3$(*p*)	2.0	165°	$C_{18}H_{14}N_2O_2S$	N :8 14	8.69

* This condensation was carried out at 140°-145°.

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METAL CHELATE COMPLEXES OF SULFOSALICYLALDEHYDE WITH POLYCYCLIC RINGS

By Ajit Kumar Mukherjee and Priyadaranjan Rây

Several metal chelate complexes of bivalent copper, nickel, cobalt and manganese, tervalent iron and of sexivalent uranium with 5-sulfosalicylaldehyde and *p*-aminophenylsulphonamide, aniline, and ethylenediamine, have been prepared and their properties studied. The configurations of these complexes closely resemble those of Pfeiffer's inner-metallic complexes of salicylaldimines. Sulfosalicylaldehyde-sulphanilamide and sulfosalicylaldehyde-aniline function as bidentate ligands. The ethylenediamine *bis*-sulfosalicylaldehyde like the corresponding Schiff's base of ethylenediamine and salicylaldehyde, behaves as a quadridentate chelating ligand. The structure of the metal chelates and the nature of the bonds involved in their formation have been elucidated from a study of their magnetic properties.

Pfeiffer and co-workers in their comprehensive work on the polycyclic complexes of oxyaldimines and oxyketimines with metallic elements (*J. prakt. Chem.*, 1937, **149**, 217 ; 1938, **151**, 145; 1940, **155**, 77 ; 1942, **159**, 313 ; *Ber.*, 1944, **77A**, 59), have discussed the most probable structures of those complexes on the basis of their physical and chemical properties. Similar types of inner-metallic complexes with different *o*-hydroxyaldehydes and amino-acids have already been described in the previous communications (this *Journal*, 1950, **27**, 707 ; 1955, **32**, 505, 567, 581, 604).

In the present communication similar types of metal chelate complexes of copper, nickel, cobalt, manganese, iron and uranium with 5-sulfosalicylaldehyde (salicylaldehyde-5-sulphonic acid) and amines or related compounds have been described. Salicylaldehyde-5-sulphonic acid possesses all the characteristics of *o*-hydroxyaldehydes. Like salicylaldehyde, it has been found to afford chelate complexes with nickel, cobalt, copper and zinc (Calvin and Melchoir, *J. Amer. Chem. Soc.*, 1948, **70**, 3270).

The Schiff's bases of 5-sulfosalicylaldehyde with sulphanilamide, aniline or ethylenediamine were obtained by the sulphonation of the corresponding Schiff's bases derived from salicylaldehyde. The metal chelates were usually prepared from these sulphonated Schiff's bases and metal acetates in aqueous alcoholic medium as usual. Owing to the presence of a free acidic—SO_3H group in these complexes, a large number of their salts with various metallic elements have been obtained. The silver salt of the copper-sulphanilamide-sulfosalicylaldehyde was obtained in two forms, differing in colour—brown and green. These are soluble in aqueous pyridine. The brown solution of the brown product changes gradually to green, while the green modification, curiously enough, forms at first a brown solution which changes finally to green. Both the varieties have the same absorbancy in aqueous pyridine in the visible region. Hence, no definite conclusion regarding the colour difference could be made. The lead salt was also obtained in two different forms, brown and green. Pfeiffer and Kreb (*loc.cit.*) also described two forms of the sodium and barium salts of the copper-salicylaldehyde-anil-4- sulphonic acid chelate complex with different water content and suggested that the difference might

arise either from dimorphism or *cis-trans* isomerism. The structure of the complexes described here and the nature of the bonds involved in their formation have been elucidated from a study of their magnetic properties.

EXPERIMENTAL

Schiff's Base : (*a*) *Sulfosalicylaldehyde-sulphanilamide*

The Schiff's base of salicylaldehyde-sulphanilamide was first prepared by the condensation of salicylaldehyde (1 *M*) and sulphanilamide (1 *M*) in hot ethanol, and the dry product (Schiff's base) was sulphonated by heating with five times its weight of H_2SO_4 (sp. gr. 1.84) in a round-bottomed flask fitted with a guard tube on the water-bath for 2 to 2½ hours with occasional shaking. The resulting light yellow mixture was then cooled in a freezing bath. Small pieces of ice were then added with constant shaking, when the compound crystallised out. These were recrystallised from hot water and dried in vacuum (H_2SO_4).

The substance forms shining yellow crystals, highly soluble in water but insoluble in various organic solvents. It is decomposed by strong alkalies and acids on warming. [Found : N, 7.69; S, 18.04. $C_{13}H_{12}O_6N_2S_2$ requires N, 7.86 ; S, 17.97 per cent].

Sulphur was estimated by precipitation as $BaSO_4$ after fusion with Na_2O_2 and Na_2CO_3. Nitrogen was estimated as usual by Kjeldhal's method.

Copper-sulfosalicylaldehyde-sulphanilamide : *Sodium Salt.*—Copper acetate (1 g.) and the Schiff's base (*a*, 3.6 g.) were refluxed in alcoholic medium on a water-bath ; sodium acetate (3 g.) and a small quantity of water were then added to the resulting mixture when a clear, deep brown solution was obtained. This was filtered hot ; the filtrate on standing deposited deep chocolate-brown, shining needles of the sodium salt.

The substance is highly soluble in water and in pyridine, but only sparingly soluble in alcohol and acetone. It is decomposed by strong mineral acids and alkalies. [Found : N, 5.89; S, 13.82; Cu, 6.68 ; Na, 4.78 ; H_2O (by loss at 110°), 13.41. $Cu(C_{13}H_{10}O_6S_2N_2Na)_2$, $7H_2O$ requires N, 5.93; S, 13.55; Cu, 6.74 ; Na, 4.87 ; H_2O, 13.33 per cent]. [Found (dried at 110°) : N, 6.86; Cu, 7.78. Calc. (anhyd.): N, 6.84; Cu, 7.76 per cent].

Barium salt was obtained as a deep brown crystalline precipitate by adding a concentrated solution of barium chloride to that of the sodium salt. The barium salt is sparingly soluble in water and alcohol, but fairly soluble in pyridine. [Found: N, 5.58; S, 12.82; Ba, 13.56; Cu, 6.33; H_2O (by loss at 110°), 9.05. Cu $(C_{13}H_{10}O_6N_2S_2)_2Ba$, $5H_2O$ requires N, 5.60 ; S, 12.81 ; Ba, 13.74 ; Cu, 6.36 ; H_2O, 9.01 per cent]. [Found (dried at 110°) : Cu, 6.99. Calc. (anhyd.) Cu: 6.99 per cent].

Calcium salt was obtained in the form of brown shining needles by evaporating a solution of calcium chloride with that of the sodium salt over H_2SO_4 (conc.) in a desiccator. It resembles the barium salt in properties [Found: N, 6.40; S, 14.45 ; Cu, 6.99; Ca, 4.52; H_2O (by loss at 112°), 8.16. $Cu(C_{13}H_{10}O_6N_2S_2)_2Ca$, $4H_2O$ requires N, 6.34 ; S, 14.48 ; Cu, 7.19 ; Ca, 4.52; H_2O, 8.15 per cent]. [Found (dried at 112°): Cu, 7.86. Calc. (anhyd.) Cu : 7.83 per cent].

Strontium salt was obtained like the previous compound, which it resembles in properties, from the sodium salt and strontium chloride. [Found : N, 6.06; S, 13.86; Cu, 6.91 ; Sr, 9 45 ; H_2O (by loss at 108°), 6.68. Cu $(C_{13}H_{10}O_6N_2S_2)_2Sr$, $3.5H_2O$ requires N, 6.07 ; S, 13.88 ; Cu, 6.90 ; Sr, 9.50 ; H_2O, 6.83 per cent]. [Found (dried at 108°): Cu, 7.42. Calc. (anhyd.) Cu: 7.40 per cent].

Zinc Salt.—From a concentrated solution of zinc acetate and that of sodium salt, green shining crystals of the zinc salt separated out on standing. The filtrate, however, yielded a green salt mixed with some brown crystalline product. The brown variety, however, could not be isolated in the pure state.

The green salt is soluble in water and in pyridine giving a deep brown solution, and is only slightly soluble in alcohol, acetone and dioxan. [Found : N, 6.44 ; S, 14.66; Cu, 7.58 ; Zn, 7.81 ; H_2O (by loss at 108°), 4.16. $Cu(C_{13}H_{10}O_6N_2S_2)_2Zn$, $2H_2O$ requires N, 6.41 ; S, 14,66 ; Cu, 7.29 ; Zn, 7 49 ; H_2O, 4.12 per cent]. [Found (dried at 108°): Cu, 7.62. Calc. (anhyd.) Cu : 7.60 per cent].

Cadmium salt was prepared as in the previous case using cadmium acetate in place of zinc acetate. It forms green crystals, soluble in water and in pyridine, but sparingly soluble in alcohol and other organic solvents. [Found : N, 5.74 ; S, 13.40 ; Cu, 6.50 ; Cd, 11.54 ; H_2O (by loss at 110°), 8.98. $Cu(C_{13}H_{10}O_6N_2S_2)_2Cd$, $5H_2O$ requires N, 5.75; S, 13.14 ; Cu, 6.53 ; Cd, 11.54 ; H_2O, 9.24 per cent]. [Found (dried at 110°) : Cu, 7.22. Calc. (anhyd.) Cu: 7.19 per cent].

Lead salt was obtained in two modifications differing in colour. A brown crystalline product was obtained as usual by the addition of lead acetate to a concentrated solution of the sodium salt of the complex acid.

The filtrate from the brown product slowly turned green and on standing deposited green crystals. The brown salt is sparingly soluble in water, but fairly so in dilute pyridine. The green salt is, however, insoluble in water and alcohol, but soluble in pyridine. [Found (brown) : Cu, 5.98 ; Pb, 19.46 ; H_2O (by loss at 105°), 8.22. $Cu(C_{13}H_{10}O_6N_2S_2)_2Pb$, $5H_2O$ requires Cu, 5.95 ; Pb, 19.38 ; H_2O, 8.42 per cent]. [Found (green) : Cu, 6.12 ; Pb, 19.75 ; H_2O (by loss at 105°), 6.90. $Cu(C_{13}H_{10}O_6N_2S_2)_2Pb$, $4H_2O$ requires Cu, 6.05 ; Pb, 19.71 ; H_2O, 6.85 per cent]. [Found (brown, dried at 105°) : Cu, 6.52 ; Calc. (anhyd.) Cu : 6.50. Found (green, dried at 105°) : Cu, 6.55. Calc. (anhyd.) Cu: 6.50 per cent].

Copper salt was obtained as green shining crystals from a concentrated solution of copper acetate and that of the sodium salt in the cold. It resembles the other salts in properties. [Found : N, 6.11 ; S, 13.88 ; Cu, 13.81 ; H_2O (by loss at 110°), 9.78. $Cu_2(C_{13}H_{10}O_6N_2S_2)_2$, $5H_2O$ requires N, 6.05 ; S, 13.83 ; Cu, 13.75 ; H_2O, 9 72 per cent]. [Found (dried at 110°) : Cu, 15.33 ; S, 15.46. Calc. (anhyd.) : Cu, 15.23 ; S, 15.32 per cent].

Silver salt of the complex acid was obtained in two modifications, differing in colour—brown and green. A chocolate-brown product was produced by the addition of silver nitrate solution to a concentrated solution of the sodium salt at the room temperature. This was filtered rapidly, and washed first with cold water, then with alcohol and finally with cold and dry ether.

The brown product is insoluble in water, alcohol, acetone, dioxan, benzene and other organic solvents; but it is fairly soluble in aqueous pyridine, giving a deep brown solution which gradually turns green at the room temperature. The brown product, if kept below 0° under water, changes to the green form, and the green form in aqueous suspension on heating turns brown. When dry, the solid brown product is, however, stable and does not turn green on cooling even below 0°.

The green variety of the silver salt was usually obtained as before by the addition of silver nitrate to a strong aqueous solution of the sodium salt at or below 0°. Both the green and brown products first separated together, but on keeping the mixture below 0° for several hours, the entire product turned green. This was washed and dried as in the previous case.

The green form resembles the brown product in properties, but furnishes a brown solution with aqueous pyridine, which finally changes to green. The maximum absorbancy of both the forms in dilute pyridine solution lies near about 420-430 mμ of the visible spectrum, but their intensities differ for the same molar concentration. [Found (brown): N, 5.64; S, 12.88; Cu, 6.37; Ag, 21 68. Found (green): N, 5.66; S, 12.88; Cu, 6.35; Ag, 21.71. $Cu(C_{13}H_{10}O_6N_2S_2Ag)_2$, $0.5H_2O$ requires N, 5.62; S, 12.84; Cu, 6.38; Ag, 21.64 per cent].

Nickel-sulfosalicylaldehyde-sulphanilamide.—Sodium salt was prepared like the sodium salt of the corresponding copper complex using nickel acetate in place of copper acetate.

The substance forms yellowish green shining crystals, highly soluble in water and in pyridine, but less soluble in alcohol, dioxan and acetone. Aqueous solution of the salt reacts with silver nitrate, barium chloride, zinc acetate and calcium chloride respectively to furnish the corresponding salt. [Found: N, 6.45; S, 14.32; Ni, 6.65; Na, 5.23; H_2O (by loss at 112°), 8.16. $Ni(C_{13}H_{10}O_6N_2S_2Na)_2$, $4H_2O$ requires N, 6.33; S, 14.47; Ni, 6.63; Na, 5.20; H_2O, 8.13 per cent.] [Found (dried at 110°): Ni, 7.24; S, 15.76. Calc. (anhyd.): Ni 7.22; S, 15.75 per cent].

Silver salt was obtained as yellow crystals by the addition of silver nitrate solution to a concentrated solution of the sodium salt in the cold. [Found: N, 5.41; S, 12.38; Ni, 5.64; Ag, 20.78; H_2O (by loss at 108°), 5.16. $Ni(C_{13}H_{10}O_6N_2S_2Ag)_2$, $3H_2O$ requires N, 5.40; S, 12.35; Ni, 5.66; Ag, 20.82; H_2O, 5.21 per cent]. [Found (dried at 108°): Ni, 5.88. Calc. (anhyd.) Ni: 5.97 per cent].

Cobalt-sulfosalicylaldehyde-sulphanilamide.—Sodium salt was obtained like the sodium salts of the corresponding copper or nickel complex using cobalt acetate in place of copper acetate or nickel acetate. It forms chocolate-brown shining needles which are highly soluble in water and in pyridine, but insoluble in alcohol, acetone, benzene and dioxan. [Found: N, 6.42; S, 14.64; Co, 6.73; Na, 5.28; H_2O (by loss at 108°), 7.12. $Co(C_{13}H_{10}O_6N_2S_2Na)_2$, $3.5H_2O$ requires N, 6.39; S, 14.61; Co, 6.73; Na, 5.25; H_2O, 7.19 per cent]. [Found (dried at 108°): Co, 7.29. Calc. (anhyd.) Co: 7.25 per cent].

Silver salt was obtained as a yellow-brown precipitate from the sodium salt and silver nitrate in water below 0°. [Found: N, 5.53; S, 12.53; Co, 5.81; Ag, 20.98;

H_2O (by loss at 108°), 3.56. $Co(C_{13}H_{10}O_6N_2S_2Ag)_2$, $2H_2O$ requires N, 5.50; S, 12.56; Co, 5.79; Ag, 21.18; H_2O, 3.53 per cent]. [Found (dried at 108°): Co, 6.04. Calc. (anhyd.) Co: 6.0 per cent].

Manganese-sulfosalicylaldehyde-sulphanilamide.—A weighed amount of manganese acetate (1 *M*) and sulfosalicylaldehyde sulphanilamide–Schiff's base (1 *M*) were refluxed in alcoholic solution on the water-bath for 1 to 2 hours; then a little water was added, just sufficient to obtain a clear solution. The resulting mixture was further refluxed for an hour and filtered hot. The orange-brown filtrate on standing deposited shining orange crystals of the manganese complex.

The substance is highly soluble in water and in pyridine, but sparingly soluble in many organic solvents. It is decomposed by dilute mineral acids on warming. With silver nitrate it gives a light brown silver salt and a brown barium salt with barium chloride. [Found: N, 6.84; S, 15.63; Mn, 6.63; H_2O (by loss at 108°), 6.61. $Mn(C_{13}H_{11}O_6N_2S_2)_2$, $3H_2O$ requires N, 6.84; S, 15.63; Mn, 6.71; H_2O, 6.59 per cent]. [Found (dried at 108°): Mn, 7.20. Calc. (anhyd.) Mn: 7.18 per cent].

Uranyl sulfosalicylaldehyde-sulphanilamide was prepared like the previous compound using uranyl acetate in place of manganese acetate. The substance forms orange-yellow crystals, highly soluble in water and in pyridine, but only sparingly soluble in alcohol, acetone, chloroform and dioxan. [Found: N, 5.63; S, 12.83; U, 23.86; H_2O (by loss at 112°), 1.81. $UO_2(C_{13}H_{11}O_6N_2S_2)_2$, H_2O requires N, 5.61; S, 12.82; U, 23.86; H_2O, 1.80 per cent]. [Found (dried at 112°): U, 24.26. Calc. (anhyd.) U: 24.30 per cent].

Ferric Sulfosalicylaldehyde-sulphanilamide Chloride.—Ferric chloride (1 *M.*) and sulfosalicylaldehyde-sulphanilamide (1 *M*) were refluxed for an hour on the water-bath. A deep violet-red solution was obtained. The resulting mixture was filtered; the filtrate on standing over H_2SO_4 (conc.) in vacuum yielded violet-red powder. This was filtered, washed with cold water and alcohol, and finally recrystallised from alcohol.

The substance is fairly soluble in water and alcohol, but less soluble in organic solvents. It dissolves in cold dilute alkalies, but is decomposed by dilute mineral acids. [Found: N, 6.48; S, 15.33; Cl, 4.27; Fe, 6.71; H_2O (by loss at 112°), 4.28. $Fe(C_{13}H_{11}O_6N_2S_2)_2$ Cl, 2 H_2O requires N, 6.69; S, 15.30; Cl, 4.23; Fe, 6.67; H_2O, 4.30 per cent]. [Found (dried at 112°): Fe, 6.92. Calc. (anhyd.)Fe: 6.9 per cent].

Schiff's Base: (*b*) *Sulfosalicylaldehyde-anil* (*or Aniline-salicylaldehyde-sulphonic Acid*)

The Schiff's base was obtained, like the corresponding sulfosalicylaldehyde-sulphanilamide, by sulphonating pure and dry Schiff's base of aniline and salicylaldehyde.

The substance (orange-yellow crystals) is highly soluble in water and in dilute pyridine and alcohol. [Found: C, 56.36; H, 3.89; N, 5.05; S, 11.36. SO_3H (OH)-C_6H_3CH : NPh requires C, 56.32; H, 3.97; N, 5.05; S, 11.55 per cent].

Copper-sulfosalicylaldehyde-anil.—Copper acetate (1 *M*) and sulfosalicylaldehyde-anil-Schiff's base (2 *M*) were refluxed in alcoholic medium for 1 to 2 hours on the water-bath. The resulting deep chocolate-brown mixture was filtered, and from the filtrate greenish brown crystals of the compound separated on standing.

The substance is highly soluble in water, but less soluble in alcohol and pyridine. It is, however, soluble in acetone, benzene, chloroform and dioxan. With silver nitrate it gives a light yellowish brown precipitate. [Found: C, 45.45; H, 3.93; N, 4.08; S, 9.32; Cu, 9.25; H_2O (by loss at 108°), 10.39. Cu $(C_{13}H_{10}O_4NS)_2$, 4 H_2O requires C, 45.37; H, 4.07; N, 4.07; S, 9.31; Cu, 9.25; H_2O, 10.47 per cent]. [Found (dried at 108°): Cu 10.34. Calc. (anhyd.) Cu: 10.33 per cent].

The *sodium salt* was obtained by evaporating a solution of the complex copper-acid with dilute caustic soda solution over H_2SO_4 (conc.) in a desiccator. It forms deep chocolate-brown crystals, soluble in water. [Found: N, 4.04; S, 9.21; Cu, 8.99; Na, 6.63; H_2O (by loss at 102°), 5.18. Cu $(C_{13}H_9O_4NSNa)_2$, 2 H_2O requires N, 4.03; S, 9.20; Cu, 9.14; Na, 6.61; H_2O, 5.18 per cent].

Nickel-sulfosalicylaldehyde-anil : Sodium Salt.—Sulfosalicylaldehyde-anil (2 *M*), nickel acetate (1 *M*) and sodium hydroxide (2 *M*) were refluxed in alcoholic medium on the water-bath for an hour, when a little water was added, and the mixture was refluxed further for half an hour. This was then filtered hot; the filtrate on standing deposited greenish yellow shining crystals of the sodium salt.

The substance is soluble in water and in pyridine, but only sparingly soluble in alcohol, acetone and dioxan. The sodium salt reacts with silver nitrate and barium chloride to yield precipitates of the corresponding silver and barium salts. [Found: C, 43.13; N, 7.67; Ni, 8.09; Na, 6.34; H_2O (by loss at 102°), 9.92. Ni $(C_{13}H_9O_4NSNa)_2$, 4 H_2O requires C, 42.94; N, 7.71; Ni, 8.08; Na, 6.33; H_2O, 9.91 per cent]. [Found (dried at 102°): Ni, 8.96. Calc. (anhyd.) Ni: 8.97 per cent].

Cobalt-sulfosalicylaldehyde-anil was obtained like the corresponding copper complex, using cobalt acetate in place of copper acetate.

It forms chocolate-brown shining crystals, fairly soluble in water, pyridine and alcohol. The crystals are, however, sparingly soluble in acetone and dioxan, and insoluble in benzene, chloroform and toluene. With silver nitrate, barium chloride, calcium chloride or zinc acetate, the substance furnishes a precipitate of the corresponding metal salt. [Found: C, 48.36; H, 3.66; N, 4.33; S, 9.91; Co, 9.02; H_2O (by loss at 102°), 5.53. Co $(C_{13}H_{10}O_4NS)_2$, 2 H_2O requires C, 48.23; H, 3.71; N, 4.33; S, 9.89; Co, 9.11; H_2O, 5.57 per cent]. [Found (dried at 102°): Co, 9.72. Calc. (anhyd.) Co: 9.65 per cent].

Manganese-sulfosalicylaldehyde-anil was prepared by heating manganous acetate (1 *M*) and sulfosalicylaldehyde-anil-Schiff's base (2 *M*) in ethanol as in the case of cobalt. This orange-red compound resembles the corresponding cobalt complex in properties. [Found: C, 48.62; H, 3.58; N, 4.34; S, 9.96; Mn, 8.56; H_2O (by loss at 105°), 5.58. Mn $(C_{13}H_{10}O_4NS)_2$, 2 H_2O requires C, 48.53; H, 3.72; N, 4.36; S, 9.96; Mn, 8.54; H_2O, 5.60 per cent].

Uranyl sulfosalicylaldehyde-anil was prepared like the corresponding copper compound using uranyl acetate in place of copper acetate. It forms orange crystals, highly soluble in water, but slightly so in alcohol. With barium chloride, zinc acetate or silver nitrate it gives a precipitate of the corresponding metal salt. [Found: C, 36.82; H, 2.58; N, 3.32; S, 7.55; U, 28.06; H_2O (by loss at 108°), 3.22. UO_2 $(C_{13}H_{10}O_4NS_2$, 1.5 H_2O

requires C, 36.74 ; H, 2.71 ; N, 3.30 ; S, 7.54 ; U, 28.04 ; H_2O, 3.18 per cent]. [Found (dried at 108°) : U, 28.89. Calc. (anhyd.) : U, 28.96 per cent].

Ferric-sulfosalicylaldehyde-anil chioride was prepared like the corresponding sulphanilamide-sulfosalicylaldehyde compound, described before, using sulfosalicylaldehyde-anil-Schiff's base in place of sulfosalicylaldehyde-sulphanilamide.

The substance forms a violet-red product, highly soluble in water and alcohol, but only slightly soluble in acetone, dioxan, ether and pyridine. [Found : C, 46.23 ; H, 3.28 ; N, 4.12 ; Cl, 5.28 ; S, 9.42 ; Fe, 8.23 ; H_2O (by loss at 105°), 5.24. Fe $(C_{13}H_{10}O_4NS)_2$ Cl, 2 H_2O requires C, 45.93; H, 3.53 ; N, 4.12 ; Cl, 5.22 ; S, 9.42 ; Fe, 8.22 ; H_2O, 5.30 per cent]. [Found (dried at 105°) : Fe, 8.72. Calc. (anhyd.) Fe : 8.68 per cent].

Schiff's Base : (c) Ethylenediamine-bis-*sulfosalicylaldehyde*

This was obtained like the corresponding sulfosalicylaldehyde-sulphanilamide or sulfosalicylaldehyde-anil, by sulphonating the pure and dry Schiff's base, ethylenediamine-*bis*-salicylaldehyde (m. p. 126-27°), with H_2SO_4 (conc.).

The substance forms shining white needles and is highly soluble in water with a light yellow colour. It is insoluble in alcohol, acetone, benzene, chloroform and dioxan, but is fairly soluble in dilute pyridine. It forms coloured complexes with nickel, cobalt, copper, manganese and uranium ions, and produces an intense violet-red coloration with ferrous or ferric ions. The copper complex, however, could not be obtained in the pure state. [Found : C, 44.88 ; H, 3.82 ; N, 6.51 ; S, 14 96. $C_{16}H_{16}O_8N_2S_2$ requires C, 44.86 ; H, 3.74 ; N, 6.54 ; S, 14.95 per cent].

Nickel-ethylenediamine-bis-*sulfosalicylaldehyde : Sodium Salt.*—Nickel acetate (1 *M*) and ethylenediamine-*bis*-sulfosalicylaldehyde (1 *M*) in hot ethanol were refluxed on the water-bath for 1 to 2 hours; the resulting mixture was then treated with the calculated amount of NaOH solution and refluxed further until a clear orange-brown solution was obtained. This was filtered hot ; the filtrate on standing deposited orange-brown crystals.

The crystals are highly soluble in water and in pyridine, but insoluble in alcohol, acetone, benzene and dioxan. [Found : C, 34.22 ; N, 4.96 ; S, 11.33 ; Ni, 10.42 ; Na, 8.16 ; H_2O (by loss at 105°), 6.42. Ni $(C_8H_6O_4NS)_2$ Na_2, 2 H_2O requires C, 34.00 ; N, 4.96 ; S, 11.33 ; Ni, 10.40 ; Na, 8.15 ; H_2O, 6.38 per cent]. [Found (dried at 105°) : Ni, 11.12. Calc. (anhyd.) Ni : 11.10 per cent].

The *barium salt* was obtained as an orange-yellow precipitate when barium chloride was added dropwise to a solution of the sodium salt. It dissolves in pyridine and strong alkalies, but is insoluble in water. [Found : N, 4.15 ; S, 9.53 ; Ni, 8.73 ; Ba, 20.33 ; H_2O (by loss at 108°), 8.03. Ni $(C_8H_6O_4NS)_2$ Ba, 3 H_2O requires N, 4.15 ; S, 9.49; Ni, 8.71; Ba, 20.38; H_2O, 8.01 per cent]. [Found (dried at 108°) : Ni, 9.48. Calc. (anhyd) Ni : 9.46 per cent].

The *silver salt* was obtained as a cream-coloured silky precipitate by adding a solution of silver nitrate to that of the sodium salt. The filtrate from the silver salt turned green in colour on long standing and yielded a green product of indefinite composition.

[Found : S, 8.68 ; Ni, 8.12 ; Ag, 30.11 ; H_2O (by loss at 105°), 3.78. Ni $(C_8H_6O_4NS)_2$-Ag_2, 1.5 H_2O requires S, 8.82 ; Ni, 8.09 ; Ag, 29.74 ; H_2O. 3.72 per cent]. [Found (dried at 105°) : Ni, 8.36. Calc. (anhyd.) : Ni, 8.40 per cent].

Cobalt-ethylenediamine-bis-*sulfosalicylaldehyde*.—The cobaltous compound was obtained like the corresponding cobalt complex of sulfosalicylaldehyde-anil using ethylenediamine-*bis*-sulfosalicylaldehyde in place of the anil base. The substance forms chocolate-brown hygroscopic crystals, highly soluble in water and in pyridine, but only sparingly soluble in alcohol and dioxan. [Found : C, 34.55 ; H, 4.16 ; N, 5.06 ; S, 11.52 ; Co, 10.58 ; H_2O (by loss at 108°), 12.98. $Co(C_8H_7O_4NS)_2$, $4H_2O$ requires C, 34.49 ; H, 3.95 ; N, 5.03 ; S, 11.49 ; Co, 10.59 ; H_2O, 12.93 per cent]. [Found : (dried at 108°) : Co, 12.26. Calc. (anhyd.) Co : 12.20 per cent].

The *sodium salt* was obtained by adding a strong solution of sodium acetate to that of the complex acid. The substance separates as chocolate-brown crystals on cooling. [Found : C, 31.18 ; H, 3.63 ; N, 4.53 ; S, 10.33 ; Co, 9.52 ; Na, 7.46 ; H_2O (by loss at 108°), 14.50. $Co(C_8H_6O_4NS)_2Na_2$, 5 H_2O requires C, 31.02 ; H, 3.56 ; N ; 4.52 ; S, 10.34 ; Co, 9.52 ; Na, 7.42 ; H_2O, 14.54 per cent]. [Found (dried at 108°) : Co, 11.16. Calc. (anhyd.) Co : 11.14 per cent].

Manganese-ethylenediamine-bis-*sulfosalicylaldehyde*.—*Sodium salt* was obtained like the sodium salt of the corresponding nickel complex, using manganese acetate in place of nickel acetate. It resembles the nickel compound in properties. [Found: C, 36.02 ; H, 2.66 ; N, 5.16 ; S, 11.82 ; Mn, 10.16 ; Na, 8.48 ; H_2O (by loss at 105°), 3.30. $Mn(C_8H_6O_4NS)_2Na_2$, H_2O requires C, 35.37; H, 2.58; N, 5.16 ; S, 11.79 ; Mn, 10.12 ; Na, 8.47; H_2O, 3.32 per cent]. [Found (dried at 105°): S, 12.16. Calc. (anhyd.) : S, 12.20 per cent].

Ferric-ethylenediamine-bis-*sulfosalicylaldehyde chloride* was prepared like the nickel compound using ferric chloride in place of nickel acetate. It forms a deep violet-red product, highly soluble in water and in pyridine, but moderately soluble in alcohol and acetone, and insoluble in benzene, chloroform, ether and toluene. It is decomposed by mineral acids on warming, but dissolves in dilute alkalies with a deep red colour. [Found : C, 36.05; H, 2.93 ; N, 5.28 ; Cl, 6.68 ; S, 12.14 ; Fe, 10.60. $Fe(C_8H_7O_4NS)_2Cl$, H_2O requires C, 35.87 ; H, 2.99 ; N, 5.23 ; Cl, 6.62 ; S, 11.96 ; Fe, 10.43 per cent].

Uranyl-ethylenediamine-bis-*sulfosalicylaldehyde* was obtained like the corresponding nickel complex using uranyl acetate in place of nickel acetate. It forms orange-yellow crystals, highly soluble in water, but moderately so in alcohol, pyridine and dioxan. With barium chloride it gives a light orange-yellow precipitate of the barium salt. [Found : N, 3.84 ; S, 8.72 ; U, 32.53 ; H_2O (by loss at 105°), 4.88. $UO_2(C_8H_7O_4NS)_2$, $2H_2O$ requires N, 3.82 ; S, 8.74 ; U, 32.52; H_2O, 4.92 per cent]. [Found (dried at 105°) : U, 34.22 ; S, 9.18. Calc. (anhyd.) : U, 34.20; S, 9.20 per cent].

Magnetic Measurements

The magnetic susceptibilities of the compounds were measured in a Gouy's balance (single-pan, semi-micro "Mettler" balance) with a field strength of 9.02×10^3 gauss. The results of measurements are recorded in Table I.

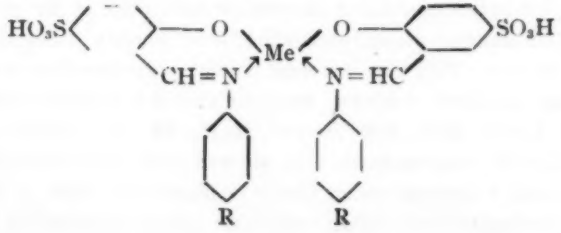
TABLE I

[SA and En denote sulfosalicylaldehyde and ethylenediamine respectively]

	Name.	Colour.	$\chi_g \times 10^6$.	$\chi_m \times 10^6$.		Temp.	μ_B.
				Obs.	Cor.		(effective).
1	Cu-SA-sulphanilamide (Sodium salt)	Brown	1.203	1134	1354 4	32°	1.82
2.	Ni-SA-sulphanilamide (Sodium salt)	Yellowish green	3.409	3016	32c5	30°	2.80
3	Co-SA sulphanilamide (Sodium salt)	Brown	8.710	7628	7811 8	31.5°	4.38
4.	Mn-SA-sulphanilamide	Orange-red	15.02	12280	12448	30.2°	5.52
5	UO_2-SA-sulphanilamide	Orange-yellow	− 0.128	−127.7	...	3°.1°	Diamagnetic
6.	Ferric-SA-sulphanilamide chloride	Violet-red	16 28	13600	13778	31.8°	5.822
7.	Cu-SA-anil	Chocolate-brown	2.032	1397	1493	30°	1.9
8	Ni-SA-anil (Sodium salt)	Greenish yellow	5 590	4072	4168.6	30°	3.19
9.	Co-SA-anil	Chocolate-brown	8.580	5550	5639	31.6°	3 72
10.	Mn-SA-anil	Orange-red	15.01	10290	10379	30°	5.03
11.	UO_2-SA-anil	Do	− 0.179	−152 0	...	30.5°	Diamagnetic
12.	Ferrice SA-anil chloride	Violet-red	19.92	13530	13639	30.3°	5 78
13.	Ni En-*bis*-SA (Sodium salt)	Orange-brown	6.27	3546	3671	30°	2.99
14.	Co-En-*bis*-SA (Do)	Chocolate-brown	1.393	862	980	30°	1.55
15.	Mn-En-*bis*-SA (Do)	Do	16.72	9076	9190	30°	4.74
16	UO_2-En-*bis*-SA	Red	− 0.104	−76.12	...	31°	Diamagnetic
17.	Ferric-En-*bis*-SA chloride	Violet-red	22.15	11860	11971	30°	5.41

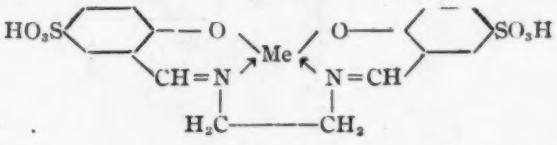
DISCUSSION

In the different complexes obtained by the interaction of sulfosalcylaldehyde-anil with different metal ions, the organic addenda behave as bidentate ligands. The Schiff's bases, sulfosalicylaldehyde-sulphanilamide and sulfosalicylaldehyde-anil, in this respect are similar to the Schiff's base, salicylaldehyde-aniline, studied by Pfeiffer and co-workers. The configuration of these complexes may thus be represented by (I)



[I : Me = bivalent metals or UO_2^{2+} ; R = H or SO_2NH_2]

In its different metal complexes the ligand, ethylenediamine-*bis* sulfosalicylaldehyde, behaves as a quadridentate chelate like the Pfeiffer's *bis*-salicylaldehyde-ethylenediamine. The compounds may therefore be represented as (II).



[II: Me = bivalent metals or UO_2^{2+}]

However, these chelate complexes differ from the corresponding metal chelates of ethylenediamine-*bis*-salicylaldehyde in respect of their physical and chemical properties, particularly the solubility, due to the presence of the free sulphonic acid group.

Copper complexes of sulfosalicylaldehyde-sulphanilamide and sulfosalicylaldehyde-anil have been found to show moment values of 1.82 and 1.92 μ_B respectively, characteristic of a planar configuration with hybrid dsp^2 bonds. The silver and lead salts of the copper chelate of sulfosalicylaldehyde-sulphanilamide were obtained in two forms, differing in colour, as already stated in the introduction.

All the nickel complexes of sulfosalicylaldehyde and different amines show paramagnetic moment values of about $3\mu_B$, corresponding to the presence of two unpaired electrons, indicating that the bonds in these complexes are of the weak covalent type with sp^3d or sp^3 covalent bonds, resonating with ionic ones. Similar results were obtained for nickel-salicylaldehyde-anil complex by Calvin and Berkelew (*J. Amer. Chem. Soc.*, 1946, **68**, 2267), though, however, they found the nickel-salicylaldehyde to be diamagnetic, and hence, of the planar structure with dsp^2 hybrid bonds.

The cobaltous complexes of sulfosalicylaldehyde with different amines gave different magnetic values. The cobalt-sulfosalicylaldehyde shows a moment value of 4.38 μ_B, closely agreeing with that of a simple cobaltous ion, and hence, possesses either a planar structure with sp^3d hybrid bond or a teterahedral structure with sp^3 hybrid bonds, resonating with ionic ones. Cobalt-sulfosalicylaldehyde-anil also behaves similarly giving a moment value of 3.72 μ_B, agreeing exactly with the theoretical spin moment of the three unpaired electrons, usually present in the cobaltous ion. The somewhat higher value of the sulphanilamide complex indicates a rather incomplete quenching of the orbital moments. The cobaltous-ethylenediamine-*bis*-sulfosalicylaldehyde chelate showed an unusual moment value of 1.55 μ_B. This low moment value, corresponding practically to the spin moment of one unpaired electron, suggests that it is a penetration complex with dsp^2 planar hybrid bonds (Rây, this *Journal*, 1948, **25**, 3). Calvin and Berkelew (*loc. cit.*) from magnetic measurement also showed that the cobalt-ethylenediamine-salicylaldehyde possessed a covalent square planar configuration with a single unpaired electron. The sulfosalicylaldehyde-ethylenediamine cobalt complex, on the other hand, has been found to exhibit no oxygen-carrying property. It shows that the presence of ethylenediamine in the ligand, as might be expected, enhances its co-ordinating

capacity, leading to the formation of complexes of the penetration type (cf. this *Journal*, 1955, **32**, 567, 581, 604).

The manganese chelate complexes of sulfosalicylaldehyde and amines have all been found to show moment values of 5.52-4.74 μ_B, more or less agreeing with that for free manganous ion. Hence, the configurations of these chelates are either planar with sp^2d or tetrahedral with sp^3 covalent bonds, resonating with ionic ones.

Uranyl chelate complexes were all found to be diamagnetic, as might be expected from the diamagnetic character of the central ion. The corresponding iron complexes all gave moment values of 5.82-5.41 μ_B. This indicates that the iron is in the ferric state and that the bonds are of the weak planar covalent type, resonating with ionic ones.

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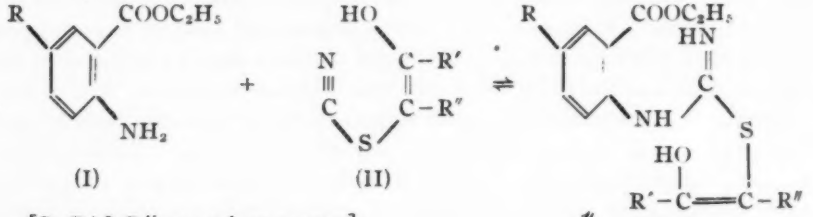
THIOPEGAN DERIVATIVES. PART VIII

By D. S. Bariana, H. S. Sachdev and K. S. Narang

Several 9 : 10-thiopegan and 6-chloro-9 : 10-thiopegan derivatives have been prepared with a view to testing their therapeutic properties. Structure of one of the two products, obtained by the condensation of ethyl 5-chloroanthranilate hydrochloride with thiocyanoacetone, has been established

Condensation of 2-carbethoxyphenylthiourea and its 4-methyl derivative with haloketones generally gave rise to 9 : 10-thiopegan derivatives except in the case of condensation with the monochloracetone, when two isomeric compounds were obtained (Narang *et al.*, *J. Sci. Ind. Res.*, 1953, **12B**, 469; *J. Org. Chem.*, 1955, **20**, 302). In view of the importance of the presence of chlorine in many chemotherapeutic compounds, it was considered desirable to sythesise 6-chloro-9 : 10-thiopegan derivatives by the old route, indicated above. However, attempted preparation of 4-chloro-2-carbethoxyphenylthiourea by the condensation of ethyl 5-chloroanthranilate hydrochloride with potassium thiocyanate under the usual conditions did not materialise, ethyl 5-chloroanthranilate having been recovered unchanged.

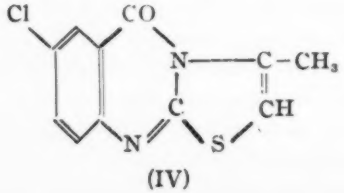
Since 2-carbethoxyphenylthiourea condenses with α-haloketones, forming ethyl anthranilate hydrochloride and α-thiocyanoketones, and as these two intermediates can further condense (Narang *et al.*, this *Journal*, 1954, **31**, 848; 1955, **32**, 631; Part VI under publication) it has been made possible to synthesise the desired 6-chloro-9 : 10-thiopegan derivatives (III) by the condensation of ethyl 5-chloroanthranilate hydrochloride (I) with various α-thiocyanoketones (II). Besides, some simple 9 : 10-thiopegan derivatives have also been prepared by the old method (Table I). These condensations generally gave rise to only one product in each case. These products have been given the general structure (III).



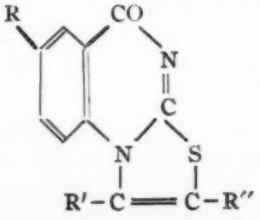
(I) (II)

[R, R′ & R″ = various groups].

(Hypothetical instermediate)



(IV)



(III)

TABLE I

9 : 10-*Thiopegan derivatives* (III).

No.	Ketones used.	Product formed. R.	R′	R″.	Yield.	Crystallistion from.	M.P.	Mol. formula.	Found.	Calc.
1.	*p*-Bromo-ω bromo-acetophenone	H	C_6H_4Br (*p*)	H	70.0%	Ethanol	263°	$C_{16}H_9ON_2BrS$	N : 7.83%	7.7%
2.	ω-Chlorobenzoin	H	C_6H_5	C_6H_5	35.0	Do	176-77°	$C_{22}H_{14}ON_2S$	S : 9 04	8.71
3.	ω-Chloroacetocatechol	H	$C_6H_3(OH)_2$	H	9 0	Acetic acid	315°	$C_{16}H_{10}O_3N_2S$	S : 10 32	10.35
4.	* Thiocyanoacetone	Cl	CH_3	H	42.0	Ethanol	160°	$C_{11}H_7ON_2ClS$	C : 52.77	52.69
					15.0	Acetic acid	315°	$C_{11}H_7ON_2ClS$	H : 2 95	2.79
5.	Methyl-ω-thiocyano-ethyl ketone	Cl	CH_3	CH_3	70 0	Ethanol	227-28°	$C_{12}H_9ON_2ClS$	S : 12.50 N : 10.4	12 77 10.6
6.	ω-Thiocyanoacatophenone	Cl	C_6H_5	H	77.0	Do	320°	$C_{16}H_9ON_2ClS$	N : 8.74 S : 10.42	8.96 10.42
7.	*p*-Methyl-ω-thiocyano-acetophenone	Cl	$C_6H_4CH_3$ (*p*)	H	68.0	Do	315°	$C_{17}H_{11}ON_2ClS$	N : 8.37	8.57
8.	*p*-Methoxy-ω-thiocyano-acetophenone	Cl	$C_6H_4OCH_3$ (*p*)	H	70.0	Do	310°	$C_{17}H_{11}O_2N_2ClS$	N : 8.12 S : 9 6	8.19 9 34
9.	*p*-Chloro-ω-thiocyano-acetophenone	Cl	C_6H_4Cl (*p*)	H	60.0	Acetic acid	340°	$C_{16}H_8ON_2Cl_2S$	Cl : 20.4	20.46
10.	*p*-Bromo-ω-thiocyano-acetophenone	Cl	C_6H_4Br (*p*)	H	70.0	Do	352°	$C_{16}H_8ON_2ClBrS$	N : 7.15	7.15

* Two isomeric compounds are formed. The compound of m.p. 160° possesses the linear structure (IV) (*loc. cit.*).

In the case of condensation of (I : R=Cl) with α-thiocyanoacetone, two products (m.p. 160° and m.p. 315°) were obtained, the former being 10 : 11-thiopegan derivative (IV), as proved by the formation of the same compound through the condensation of 5-chloroanthranilic acid with 2-chloro-4-methylthiazole (Part IX, this *issue* p. 647).

EXPERIMENTAL

Ethyl 5-Chloroanthranilate Hydrochloride.—A solution of 5-chloroanthranilic acid (50 g.) in absolute ethanol (200 c.c.) containing H_2SO_4 (conc., 30 c.c.) was refluxed for 8 hours. After distilling off the solvent the residue was made alkaline with sodium carbonate solution, and the ester repeatedly extracted with ether. The ethereal extract after drying (Na_2SO_4) was treated with dry HCl gas. The precipitated hydrochloride was collected on suction and washed with dry ether, m.p. 146°, yield 58 g. It crystallised from acetone in fine needles, m.p. 148°. (Found: N, 5.69. $C_9H_{11}O_2NCl_2$ requires N, 5.9 per cent).

The hydrochloride on basification with sodium carbonate furnished ethyl 5-chloroanthranilate which crystallised from dilute ethanol in colorless needles, m.p 82°. (Found: N, 7.02. $C_9H_{10}O_2NCl$ requires N, 7.02 per cent).

6-Chloro-9 : 10-thiopegan derivatives (III : R=Cl) were obtained by refluxing alcoholic solutions of equivalent amounts of ethyl 5-chloroanthranilate hydrochloride and α-thiocyanoketones for 6 hours. Generally, some of the products started separating during the course of refluxing. The product was collected after cooling and the free base was obtained by treatment with sodium carbonate solution. The alcoholic filtrate on dilution with water and basification generally gave the same product as obtained from the solid, mentioned above. Only in the case of condensation of the ester with thiocyanoacetone, two isomeric products, m.p. 160° and 315°, were obtained (Table I).

9 : 10-Thiopegan derivatives (III : R=H) were obtained by refluxing alcoholic solutions of 2-carbethoxyphenylthiourea with equivalent quantities of ω-4-dibromoacetophenone, α-chlorobenzoin or chloroacetocatechol for 10 to 12 hours. Solid separated out in case of the condensation with ω-4-dibromoacetophenone during refluxing, whereas in the case of chlorobenzoin the product was precipitated by the addition of ether to the cooled alcoholic solution; in the case of condensation with chloroacetocatechol, there was no separation of any solid even on removal of the solvent. The bases were liberated by the treatment of the solids in the first two cases and of the concentrate in the third case with sodium carbonate solution.

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THIOPEGAN DERIVATIVES. PART IX

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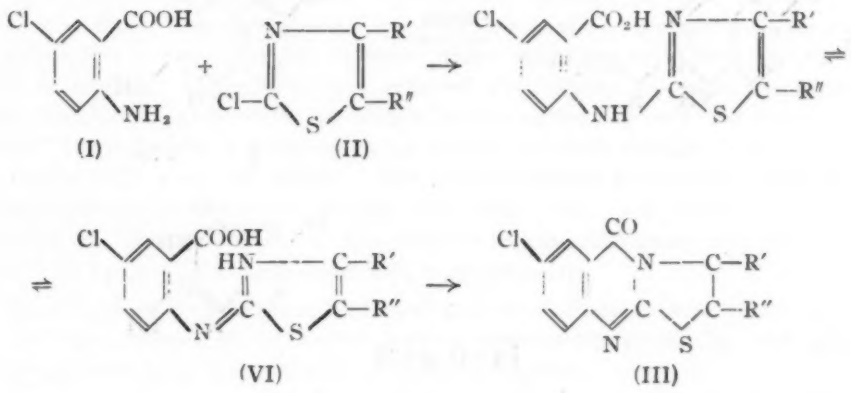
Several 10 : 11-thiopegan derivatives have been synthesised. 2-Thio-4-keto-6-chlorotetrahydroquinazoline has been synthesised and condensed with various ω-bromoacetophenones and bromomalonic ester with a view to obtaining products of chemotherapeutic value.

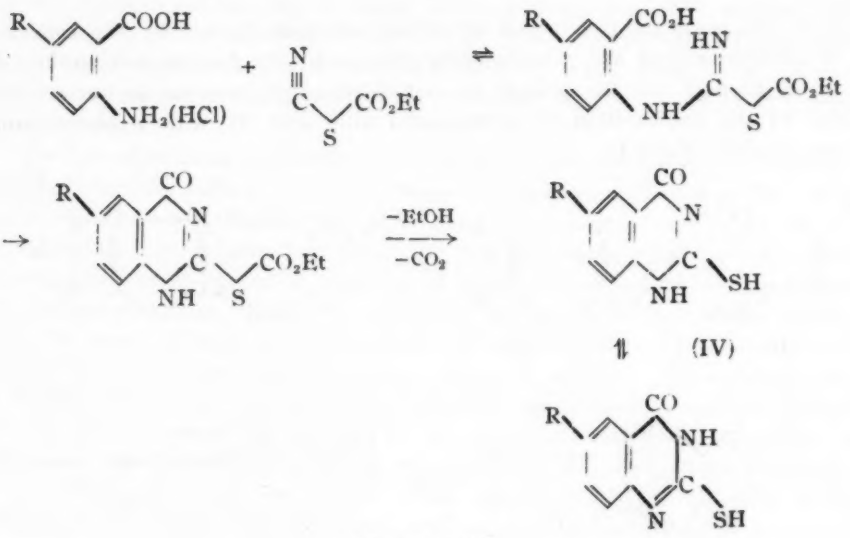
10 : 11-Thiopegan and its 6-methyl derivatives have been obtained by the condensation of anthranilic acid and 5-methylanthranilic acid with various 2-chlorothiazoles (this *issue*, p. 644). In the present paper 6-chloro-10 : 11-thiopegan derivatives (III), obtained by the condensation of 5-chloroanthranilic acid (I) with 2-chlorothiazoles (II), are described (Table I).



[R′, R ′ = various groups]

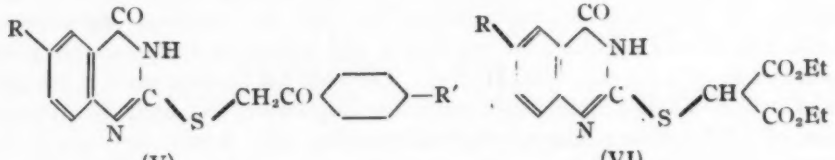
4-Keto-3 : 4-dihydro-2-mercaptoacetophenones and esters were obtained by the condensation of 2-thio-4-ketotetrahydroquinazoline and its 6-methyl derivative with ω-haloacetophenones and esters for conversion into thiopegan derivatives by cyclisation (Narang *et al.*, this *Journal*, 1954, **31**, 787). The work has been extended to the preparation of 6-chloro-4-keto-3 : 4-dihydro-2-mercaptoacetophenones and esters by the condensation of 2-thio-4-keto-6-chlorotetrahydroquinazoline (IV, R = Cl) with various ω-haloacetophenones and esters. Previously 2-thio-4-ketotetrahydroquinazoline and its 4-methyl derivatives were obtained by the cyclisation of the respective 2-carbethoxyphenylthioureas. Since 2-carbethoxy-4-chlorophenylthiourea could not be obtained by the condensation of ethyl 5-chloroanthranilate hydrochloride with potassium thiocyanate (Part VIII, *loc. cit.*), an alternative route for the synthesis of (IV, R = Cl) has been investigated. On refluxing 5-chloroanthranilic acid and potassium thiocyanate in alcoholic solution containing a small amount of hydrochloric acid, (IV : R = Cl) was obtained, but the yield was only 20 %. The formation of the above in this experiment

obviously could take place through the cyclisation of the intermediate, 2-carboxy-4-chlorophenylthiourea. Anthranilic acid condensed with ethyl thiocyanoformate in presence of hydrochloric acid to yield 50.0 % of the 2-thio-4-ketotetrahydroquinazoline (Dhatt and Narang, this *Journal*, 1954, **31**, 790) along with a small amount of a by-product (which is under investigation). The extension of this method furnished (IV: R=Cl) in 43.0% yield. The reaction is parallel to the condensation of ethyl anthranilate hydrochloride or 5-chloroanthranilic acid hydrochloride with thiocyanoketones (Narang *et al.*, *loc. cit.*, 1954, 1955); its proposed mechanism is shown below:



[R=H or Cl]

The compound (IV: R=Cl) has been condensed with α-haloketones and monobromomalonic ester with the formation of products (V) and (VI) (Table II).



[R=Cl; R′=various groups.]

EXPERIMENTAL

6-Chloro-10:11-thiopegan Derivatives.—Equivalent quantities of 5-chloroanthranilic acid and various 2-chlorothiazoles were heated in an oil-bath at 170°-180° for 1½ hours. The products in each case were warmed with ethanol (15-20 c.c. for each gram

of 5-chloroanthranilic acid in the reaction) and made alkaline with sodium carbonate solution. The products, which invariably separated out as light brown solids, were collected, washed with water and crystallised from the solvents, recorded in Table I.

TABLE I

Formation of 6-chloro-10 : 11-thiopeg-2 : 9-diene-4-ones (III).

No.	2-Chlorothiozoles used.	Product R′.	Product R″.	Yield.	Crystallised from	M.P.	Mol. formula.	%Nitrogen. Found.	%Nitrogen. Calc.
1.	-4-phenyl-	C_6H_5	H	27.0%	Acetic acid	180°	$C_{16}H_9ON_2ClS$	8.7	8.96
2.	-4-(*p*-methylphenyl)-	$C_6H_4CH_3$	H	20.0	Ethanol	211 12°	$C_{17}H_{11}ON_2ClS$	8.55	8.50
3.	-4-(*p*-methoxyphenyl)-	$C_6H_4OCH_3$	H	20.0	Do	180°	$C_{17}H_{11}O_2N_2ClS$	8.0	8.17
4.	-4-(*p* chlorophenyl)-	$C_6H_4Cl(p,$	H	30.0	Acetic acid	240°	$C_{16}H_8ON_2ClS$	8.1	8.07
5	-4-(*p*-bromophenyl)-	$C_6H_4Br(p)$	H	20.0	Do	255°	$C_{16}H_8ON_2ClSBr$	7 18	7.15
6.	-4 :5-dimetLyl-	CH_3	CH_3	50.0	Ethanol	155°	$C_{12}H_9ON_2ClS$	10.8	10.58
7.	-4-methyl-5-carbethoxy-	CH_3	$COOC_2H_5$	60.0	Acetic acid	168 69°	$C_{14}H_{11}O_3N_2ClS$	8 4	8.60

2-*Thio-4-keto-6-chlorotetrahydroquinazoline.*—A solution of 5-chloroanthranilic acid (2 g.) and potassium thiocyanate (1.1 g.) in ethanol (30 c.c.) containing HCl (1.5 g.) was refluxed on a water-bath for 12 hours. Some separation took place during the course of heating. The product was collected after cooling, triturated with aqueous sodium bicarbonate to remove the unchanged 5-chloroanthranilic acid and collected on suction. It was purified by dissolving in 2% sodium hydroxide solution (30 c.c.) which was treated with norit and filtered. The clear filtrate was acidified with acetic acid, the white precipitate collected and washed with water, m.p. 328°, yield 20.0%. On crystallisation from acetic acid it was obtained in small colorless crystals, m.p. 335°. (Found : N, 13.13. $C_8H_5ON_2Cl$ requires N, 13.17 per cent).

Since the above yield was low, the following alternative method was worked out at first for the synthesis of the known 2-thio-4-ketotetrahydroquinazoline and subsequently extended to the preparation of the 6-chloro derivative.

Potassium thiocyanate (7 g.) was added to a solution of ethylchloroformate (9 g.) in ethanol (20 c.c.), and the mixture was refluxed for ten minutes. At first a clear solution was obtained but subsequently potassium chloride started separating. A solution of anthranilic acid (10 g.) in ethanol (30 c.c.) containing HCl (conc., 1 c.c.) was then added to the above solution and the mixture refluxed for 8 hours during which period some of the product separated out. After cooling, the product was collected and treated with aqueous sodium bicarbonate solution to remove the unchanged anthranilic acid. The residue was dissolved in 2% sodium hydroxide solution (90 c.c.), clarified with norit and filtered. The white precipitate obtained by acidifying the filtrate with acetic acid in the cold was collected and washed with water (yield 7.7 g.). Crystallisation from glacial acetic acid afforded colorless crystals, m.p. 315°, identical with 2-thio-4-ketotetrahydroquinazoline (*loc. cit*). The alcoholic filtrate after removal of the solid, mentioned above, was concentrated and then diluted with water. This afforded a small amount of a byproduct which is under investigation. This method was extended to the preparation of 2-thio-4-keto-6-chlorotetrahydroquinazoline (IV : R=Cl) in 40 % yield by using 5-chloroanthranilic acid instead of anthranilic acid in the above case.

The product so obtained was found to be identical with (IV: R=Cl) as obtained by the first method, described above.

ω-4-Keto-3 : 4-dihydroquinazolyl-2-mercaptoacetophenones (V) *or the Ester* (VI).—2-Thio-4-keto-6-chlorotetrahydroquinazoline (1.06 g., 0.05 *M*) was dissolved in 10.6 c.c. of 2% NaOH solution (0.05*M*). This was diluted with 30 c.c. of water and filtered. To the clear filtrate was added dropwise an alcoholic solution of the ω-bromoacetophenones or bromomalonic ester (0.05 *M*) using 20-25 c.c. of ethanol per g. of the bromo compounds. Precipitation of the products started almost immediately. After allowing to stand for one hour with occasional shaking, the products were collected and crystallised from ethanol (Table II).

TABLE II

Condensatson of 6-chloro-4-keto-2-thiotetrahydroquinazoline.

Reacted with	R.	R′.	Yield	Solvent.	M.P.	Mol. formula	Found.	Calc.
				With ω-bromoacetophenones (Product V).				
ω-Bromoacetophenone	Cl	H	80%	Ethanol	215°	$C_{16}H_{11}O_2N_2ClS$	N : 8.5 %	8.47 %
p-Methyl-ω-bromoacetophenone	Cl	CH_3	90	,,	210°	$C_{17}H_{13}O_2N_2ClS$	N : 7.95	8.12
p-Methoxy-ω-bromoacetophenone	Cl	OCH_3	82	,,	210-11°	$C_{17}H_{13}O_3N_2ClS$	S : 7.95	7.76
p-Chloro-ω-bromoacetophenone	Cl	Cl	90	,,	265°	$C_{17}H_{11}O_2N_2Cl_2S$	Cl : 19.1	18.8
				With bromomalonic ester (Product VI).				
Bromomalonic ester	Cl	...	78	Ethanol	215°	$C_{15}H_{15}O_5N_2ClS$	N : 7.72	7.5

The authors wish to express their thanks to Dr. S. M. Mukherji for his kind interest in the work.

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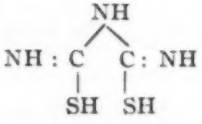
INTERACTION OF THIOAMIDES WITH METALLIC IONS AND THEIR ANALYTICAL APPLICATIONS: DITHIOBIURET AND THIOAMMELINE

By Debabrata Bandyopadhayay (Banerjea)

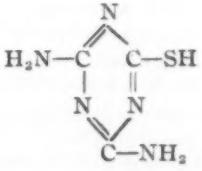
The reactions of dithiobiuret and of thioammeline with metallic ions have been investigated. Both these thioamides have been found to afford coloured precipitates with most of the metallic ions of the hydrogen sulphide groups, at suitable p_H values; the precipitates obtained with dithiobiuret are, however, very unstable and decompose readily into the sulphides. Precipitation of copper by thioammeline from acid solutions of copper salts, at a fairly low p_H (3–3·5), has been made use of for its separation from cadmium, zinc and nickel.

Many thioamides containing the reactive group $-C(SH):N-$ have been utilised as very useful analytical reagents both for the purpose of obtaining insoluble precipitates or soluble coloured products with many metallic ions (Yoe and Overholser, *Ind. Eng. Chem. Anal. Ed.*, 1942, **14**, 435). Mention may specially be made in this connection of the use of thiourea for the colorimetric estimation of bismuth (Mahr, *Z. anal. Chem.*, 1933, **94**, 161; 1934, **97**, 96) and as a masking agent for Hg, Cu and Ag in many analytical procedures (Rây and Sarkar. *Mikrochem.*, 1939, **27**, 64; Rây and Dutt, *Z. anal. Chem.*, 1939, **115**, 265), of dithio oxamide or rubeanic acid, $HN:C(SH).C(SH):NH$, for the detection of copper, nickel and cobalt (Rây and Rây, this *Journal*, 1926, **3**, 118; Rây, *Z. anal. Chem.*, 1929, **79**, 94) and for the colorimetric estimation of copper (Kisser and Lettmayr, *Mikrochem.*, 1933, **12**, 235) and of ruthenium (Welcher, "Organic Analytical Reagents", Vol. IV, p. 154, D. Van Nostrand Co., Inc., N. Y., 1948), as also of oxanilic acid thioamide, $C_6H_5.NH.CO.C(SH):NH$, for the precipitation of copper, nickel and cobalt (Majumdar, this *Journal*, 1941, **18**, 415). Mercaptobenzothiazole (Spacu and Kuras, *Z. anal. Chem.*, 1935, **102**, 24, 108) and dimercaptothiobiazole or bismuthol (Rây and Gupta, this *Journal*, 1935, **12**, 308; Dubsky and Okac, *Z. anal. Chem.* 1934, **96**, 267) afford further examples of some commonly used organic reagents of the same category.

Both dithiobiuret and thioammeline contain the reactive grouping of the thioamides and might therefore be expected to furnish useful analytical reactions with metallic ions. The structures of these substances are represented below :



(Dithiobiuret)



(Thioammeline)

Both these substances have been found to form coloured precipitates with most metals of the hydrogen sulphide groups, at suitable p_H values, but the precipitates obtained with dithiobiuret are, however, much less stable and decompose readily, forming the sulphides,

more particularly in alkaline medium. Another characteristic difference between the two is to be noted in their behaviour towards silver nitrate solution, which is readily reduced by dithiobiuret, but forms a white precipitate with thioammeline, which is insoluble in dilute nitric acid and in ammonia solutions. Copper is quantitatively precipitated by both these reagents in fairly acidic medium, and under this condition none of the other metals like lead^{II}, bismuth^{III}, cadmium, antimony^{III}, tin^{II}, zinc, manganese^{II}, cobalt^{II} and nickel^{II} is precipitated. Quantitative separation of copper from cadmium, zinc and nickel has actually been achieved by precipitating copper with an excess of thioammeline at a p_H of 3.0-3.5 (Tables I—II). For the separation from cadmium reprecipitation has been found necessary, if the weight of cadmium in the solution exceeds twice that of copper (cf. Table I). Since the copper precipitate offers no definite composition, it is decomposed by heating with a mixture of nitric and sulphuric acids to fumes, and then copper is estimated iodimetrically as usual. In the filtrates the other metals were estimated by usual procedures, after decomposing the organic matter.

Experimental

Reactions of Dithiobiuret with Metallic Ions.—A pure sample of the substance was kindly supplied by R. W. Hakala of the Pennsylvania State College, U.S.A. through Prof. P. Rây for which author's grateful thanks are due to him. It is a toxic, white solid, insoluble in cold water, slightly soluble in hot water and somewhat more in alcohol, but is readily soluble in dilute alkalies. A saturated alcoholic solution of the substance was used for studying its reactions with various metallic ions, with the observations noted below.

Table I

Ions.	Reactions.
Cu^{2+}	It forms a yellow precipitate in acid solution. Precipitation is quantitative at p_H of about 2. The precipitate is insoluble in dilute acetic acid and in small amounts of mineral acids; it turns black by alkali, or on washing with hot water or when dried, due to the formation of Cu_2S.
Hg^{2+}	It forms a white crystalline precipitate in acid solution which turns black with alkali.
Ag^{+}	Reduction to black metallic silver, change being accelerated by alkali.
Pb^{2+}	Reddish brown and finally black precipitate in alkaline medium.
Cd^{2+}	White precipitate in presence of NH_4Cl in ammoniacal medium Colour of the precipitate changes to yellow on warming.
Bi^{3+}	Bismuth nitrate gives a red precipitate in acid solution at p_H of about 3. The precipitate turns black on adding alkali.
Sb^{3+}	Light yellow precipitate in alkaline medium.
Sn^{2+}	White precipitate in ammoniacal solution. Colour of the precipitate changes to yellow with NaOH and dissolves in excess of the latter.
Zn^{2+}	White precipitate in presence of NH_4Cl in ammoniacal medium.
Mn^{2+}	Yellow precipitate in alkaline medium which is difficultly soluble in ammonia solution.
Ni^{2+}	Reddish brown precipitate in presence of NH_4Cl in ammoniacal solution and is soluble in excess of the latter.
Co^{2+}	Brownish black precipitate in presence of NH_4Cl in ammoniacal solution which is soluble in excess of the latter.
Fe^{3+}	Greenish black precipitate in alkaline medium.

Preparation of Thioammeline.—This was prepared by condensing dicyandiamide with thiocyanic acid in alcoholic solution (Williams, "Cyanogen Compounds", p. 32, Edward Arnold & Co., 1948; cf. Rathke, *Ber.*, 1885, **18**, 3102). A dilute alcoholic solution of thiocyanic acid was prepared by treating an alcoholic suspension of pure and dry $Pb(SCN)_2$ with H_2S in an ice-bath, removing the excess of H_2S by adding some more $Pb(SCN)_2$ with stirring in the cold, and then filtering off the PbS along with the excess of the $Pb(SCN)_2$. This alcoholic solution of thiocyanic acid was refluxed for three to four hours with the requisite quantity of dicyandiamide [equal to the molar proportion of thiocyanic acid, calculated on the basis of $Pb(SCN)_2$ taken]. A white crystalline precipitate separated gradually during the reaction. The liquid was cooled and the solid product was filtered off and purified by dissolving in dilute aqueous ammonia and then precipitating it with the addition of acetic acid, in which the substance was insoluble.

The substance is very sparingly soluble in cold water, somewhat more in hot water, but readily dissolves in dilute mineral acids, alkalies and aqueous ammonia. The reactions of this substance with various metallic ions are reported below.

TABLE II

Reactions of thioammeline with metallic ions

Ions.	Reactions.
Cu^{2+}	Yellow precipitate in acid solution. In 0.001 *M* solution of Cu ion the p_H's of incipient and complete precipitations are 2.02 and 2.37 and over respectively. The precipitate is soluble in dilute mineral acids, but completely insoluble in hot water.
Hg^{2+}	Mercuric chloride gives a white crystalline precipitate in acid solution; complete precipitation at 2.0—2.5 p_H. Mercuric nitrate gives a similar precipitate.
Ag^{+}	White crystalline precipitate in acid solution, which is insoluble in dilute nitric acid or in aqueous ammonia.
Cd^{2+}	Light yellow precipitate in alkaline medium.
Bi^{3+}	Light yellow precipitate in acid solution of $BiCl_3$ at about p_H 3. Bismuth nitrate gives a yellow precipitate only in the presence of a chloride.
Zn^{2+}	White precipitate at about p_H 6. The precipitate is soluble in ammonia.
Mn^{2+}	White crystalline precipitate in presence of NH_4Cl in ammoniacal medium (p_H 9 approximately).
Ni^{2+}	Yellow crystalline precipitate at p_H 5.5—6.0; soluble in acids and in ammonia.
Co^{2+}	Brick-red crystalline precipitate at p_H 5.5—6.0; soluble in acids and in ammonia.
Fe^{3+}	Light buff-coloured precipitate at p_H 7-8.
Pb^{2+}	Light yellow precipitate in acid solution. Complete precipitation at and over 2.0—2.5 p_H.

Separation of Copper from Cadmium.—The mixed solution containing copper nitrate and cadmium sulphate, of exactly known quantities, was neutralised with ammonia and then weakly acidified with hydrochloric acid. The solution was warmed on the water-bath and treated with an excess (0.2 g. for 30—40 mg. Cu.) of the reagent (1% solution in 0.2 *N*-HCl), and the p_H of the resultant mixture was adjusted thereafter to 3.0—3.5 by adding dilute KOH solution. The mixture was allowed to stand at room temperature for a few minutes in order to allow the precipitate to settle.

The precipitate was then filtered off on a quantitative filter paper and thoroughly washed with hot water. This was afterwards decomposed by heating with nitric and sulphuric acids to fuming, and copper was estimated iodimetrically as usual. In the combined filtrate and washings cadmium was estimated gravimetrically as the oxinate, after decomposing the organic matter by fuming with sulphuric acid. The results of some of the determinations are recorded in Table III. From the table it can be readily found that the separation of copper from cadmium is quantitative only when the amount of cadmium does not exceed double the weight of copper present. With larger amounts of cadmium, some cadmium is co-precipitated with the copper and a reprecipitation becomes necessary.

TABLE III

Separation of copper from cadmium.

No.	Metals present.		Metals found.	Error. (mg.)	No.	Metals present.		Metals found.	Error. (mg.)
1.	Cu	0.03299 g.	0.03299 g.	±0	4.	Cu	0.01649 g.	0.01649 g.	±0
	Cd	Nil	...			Cd	0.03256	0.03263	+0.07
2.	Cu	0.06598	0.06579	−0.19	5.	Cu	0.01649	0.01649	±0
	Cd	0.06501	0.06501	±0		Cd	0.03763	0.03657	−1.06
3.	Cu	0.04049	0.04949	±0	6.	Cu	0.01649	0.01649	±0
	Cd	0.01612	0.01603	−0.09		Cd	0.04838	0.04765	−0.73
					7.	Cu	0.01649	...	...
						Cd	0.08063	0.07754	−3.09

Similarly copper has been separated from zinc and nickel. Here the separation is quantitative in mixtures containing copper and zinc or nickel in varying proportions. The results are summarised in Table IV. Zinc has been estimated gravimetrically as zinc oxinate and nickel as nickel-dimethylglyoxime, after decomposing the organic matter by fuming with sulphuric acid.

TABLE IV

Separation of copper from zinc and nickel.

No.	Metals present.		Metals found.	Error (mg.)	No.	Metals present.		Metals found.	Error (mg.)
1.	Cu	0.03299 g.	0.03308 g.	+0.09	5.	Cu	0.01649 g.	0.01649 g.	±0
	Zn	0.00512	0.00516	+0.04		Zn	0.09267	0.09274	+0.07
2.	Cu	0.03299	0.03299	±0	6.	Cu	0.03299	0.03299	±0
	Zn	0.01075	0.01077	+0.02		Ni	0.03761	0.03762	+0.01
3.	Cu	0.03299	0.03299	±0	7.	Cu	0.03299	0.03290	−0.09
	Zn	0.03072	0.03071	−0.01		Ni	0.01317	0.01320	+0.03
4.	Cu	0.01649	0.01659	+0.10	8.	Cu	0.03299	0.03299	±0
	Zn	0.06144	0.06153	+0.09		Ni	0.09328	0.09336	+0.08

The author wishes to acknowledge gratefully his indebtedness to Prof. P. Rây for kindly providing him with all the facilities of the laboratory during the course of this work.

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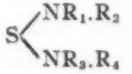
S-SUBSTITUTED THIOUREAS AS ANALYTICAL REAGENTS. PART I. S-METHYLTHIOUREA SULPHATE AS A REAGENT FOR COPPER AND NICKEL

By Sushil Kumar Siddhanta and Phatic Chandra Kundu

In alkaline solution *S*-methylthiourea sulphate slowly decomposes to yield methylmercaptan and the reaction has been utilised in this work to precipitate quantitatively nickel as nickel methylmercaptide from ammoniacal nickel solutions, and copper as cuprous methylmercaptide from ammoniacal solutions or alkaline tartrate solutions of cupric salts. The precipitates of nickel and cuprous methylmercaptides after filtration and washing can be dried to their respective stoichiometric compositions at 100°.

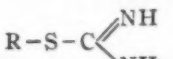
Copper-nickel and copper-zinc separations have also been found possible since copper can be quantitatively precipitated as cuprous methylmercaptide (*i*) from ammoniacal nickel solutions containing sufficient amount of ammonium oxalate and (*ii*) from ammoniacal zinc solutions containing adequate amount of ammonium chloride. Double precipitation is, however, necessary in either case to effect a complete separation. Cuprous methylmercaptide can be weighed as such; nickel can be estimated by dimethylglyoxime, and zinc as pyrophosphate from the two respective filtrates.

Thiourea has found numerous applications in analytical chemistry (Welcher, "Organic Analytical Reagents", Vol. IV, 1948, Van Nostrand Co., pp. 177-188). However, the application of substituted thioureas in chemical analyses are rather few, and the only studies in this direction appear to be those of Steiger (*Microchem.*, 1934-35, **16**, 193) and those of Yoe and Overholser (*Ind. Eng. Chem. Anal. Ed.*, 1942, **14**, 435). These studies are more or less qualitative and limited to the determination of sensitiveness of colour reactions of a large number of substituted thioureas with almost all metallic ions. Moreover, all the thiourea derivatives, studied either by Steiger or by Yoe and Overholser (*loc. cit.*), are *N*-substituted, e.g.,



where R_1, R_2, R_3 and R_4 may be any monovalent organic radical or a H-atom.

Thiourea, in its tautomeric *iso*thiourea form, can, however, form *S*-substituted derivatives, e.g.,



(R being monovalent organic radical) which have not yet been applied to analytical chemistry. In the present work, *S*-methylthiourea sulphate has been successfully employed as a gravimetric reagent for copper and nickel.

Thiourea is a weak mono-acid base forming a hydrochloride, $CS(NH_2)_2.HCl$, which loses HCl even at room temperature. The dissociation constant of the base thiourea at 25° is given by K_b (thiourea) $= 1.1 \times 10^{-15}$ (International Critical Table).

S-Substituted thioureas also behave as mono-acid bases but are much stronger than thiourea itself, as indicated by great stability of their salts with strong acids.

Employing the indicator method, we have determined the p_H of an $N/10$ solution of *S*-methylthiourea sulphate to be 4.6 at 30°, whence the value for the dissociation constant of the *S*-methylthiourea base comes out as $K_b = 1.6 \times 10^{-6}$ at 30°, using the Henderson relation: $p_H = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$. The free *S*-methylthiourea base can therefore be liberated from its sulphate by treating the latter with stronger bases, even by ammonia [K_b (ammonia) $= 1.8 \times 10^{-5}$ at 25°]. The isolation of the free base is, however, extremely difficult (Arndt, Milde and Eckert, *Ber.*, 1921, **54B**, 2236), as it decomposes even in solutions to yield methylmercaptan and polymerised products of cyanamide (e.g. dicyandiamide) :

$$RSC(=NH)NH_2 \rightleftharpoons RSH + CN.NH_2 \text{ (in polymerised state)} \quad \ldots (1)$$

The decomposition becomes very rapid on warming or on attempting to concentrate the solution otherwise.

In presence of metal ions like Pb^{2+}, Hg^{2+}, Ag^{+} etc., the desulphurisation of *S*-alkylthioureas is very rapid (almost instantaneous), particularly when the medium is alkaline.

$$M^{2+} + 2\,RSC(=NH)NH_2 \rightleftharpoons \underset{\text{(metallic mercaptide)}}{M(SR)_2} + 2H^{+} + 2\,CN.NH_2 \quad \ldots (2)$$

The forward reaction proceeds more or less towards completion due partly to the precipitation of the insoluble metallic mercaptide and partly to the removal of H^{+} ions by the alkaline medium.

In the present work, nickel and cuprous methylmercaptides, $Ni(SCH_3)_2$ and $Cu(SCH_3)$, have been obtained as extremely insoluble substances by adding *S*-methylthiourea sulphate to strongly ammoniacal solutions of nickel or cupric salts, or to an alkaline cupri-tartrate solution*. Evidently in the case of copper, the base *S*-methylthiourea first reduces it to the cuprous condition (the reduction of cupric ion to cuprous condition by thiourea is quite well known), and then the cuprous ion formed desulphurises further amount of the base. Under suitable conditions (vide Experimental), the precipitation of cuprous and nickel methylmercaptides is quantitative and the precipitates are stable enough to be dried at 100° to their respective stoichiometric compositions.

From a medium of low ammonia concentration nickel is not precipitated at all by the reagent, and in the case of copper, black CuO is precipitated on heating. If the medium contains much ammonium salts, in addition to ammonia, the precipitation of the metallic mercaptides becomes slow.

* Although some of the methylmercaptides of lead, mercury, bismuth and silver (Klason, *Ber.*, 1887, **20**, 3410) have been described, there appears to be no mention of nickel and copper methylmercaptides in literature.

S-Methylthiourea sulphate does not produce any precipitate when added to ammoniacal nickel in presence of a large excess of ammonium oxalate (2.5 g. for each 0.1 g. of nickel) which increases the $[H^+]$ of the medium and decreases the $[Ni^{2+}]$ as well by forming a nickel oxalato-complex; copper, however, is quantitatively precipitated, and hence, a separation of copper from nickel as cuprous methylmercaptide has been possible.

Double precipitation is, however, necessary to effect a quantitative separation of copper from nickel with the help of the reagent. From the filtrate, nickel can be estimated by dimethylglyoxime.

Using the reagent, a separation of copper as cuprous methylmercaptide from zinc in a strongly ammoniacal solution containing ammonium chloride has also been found possible, as zinc is not precipitated under this condition. Zinc, however, shows some tendency for co-precipitation with $CuSCH_3$; this tendency has been observed to decrease if sufficient ammonium chloride be present. However, to effect a complete separation of copper from zinc, double precipitation is necessary. The zinc can be estimated from the filtrate as pyrophosphate.

The estimation of copper and nickel by the reagent is rapid and takes time, a little more than two hours, for completion when the metal is present singly. Some very excellent reagents, such as dimethylglyoxime for nickel, thionalide for copper and nickel, possess low solubilities in water, and can be washed off from the precipitate only with great difficulty. The reagent, S-methylthiourea (base or sulphate), possesses a high solubility and can be washed off very easily.

Some of the best reagents, like sodium quinaldinate for copper, dimethylglyoxime for nickel etc., are very costly and difficult to be prepared, whereas the preparation of S-methylthiourea sulphate is very simple and the cost is much lower; the reagent is very stable as well.

Excepting sodium quinaldinate (Rây and Sarkar, *Microchem.*, 1939, **27**, 64; Rây and Dutta, *Z. anal. Chem.*, 1939, **115**, 265) and 8-hydroxyquinoline (Calvet, *Compt. rend.*, 1932, **195**, 148), S-methylthiourea sulphate compares very well with other reagents for copper, separation of zinc being better than the latter in many respects. Again, with the exception of sodium quinaldinate (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400) and dimethylglyoxime (Grossmann and Mannheim, *Z. angew. Chem.*, 1918, **30**, 159), which are rather costly, S-methylthiourea sulphate is perhaps better than all others in copper-nickel separation in quickness, simplicity of procedure and low cost.

Among the chief demerits of the reagent, mention may be made of the liberation of mercaptan, which has a very obnoxious smell. Also to separate copper from nickel or zinc, double precipitation is necessary which is rather a time-consuming process. The sulphur-containing organic reagents used so far for the precipitation of metal ions are all structurally very complicated (mostly heterocyclic) and a few of them (thionalide, mercaptobenzothiazole) contain mercapto groups. Almost all of them contain more than one atom of sulphur in the molecule, and the precipitates obtained with the metal ions are easily oxidised at the drying temperature of 100° or so, and

therefore cannot be directly weighed. *S*-Methylthiourea sulphate (this work) and thionalide (Umemura, *J. Chem. Soc., Japan*, 1940, **61**, 25), however, yield directly weighable precipitates, indicating that the sulphur atom in metallic mercaptides is not so much susceptible to oxidation at 100° or so. It may be pointed out that thionalide like methylmercaptan has only one S atom in the molecule forming an -SH group, and this indicates that the employment of mono-mercaptans (which can easily be liberated from the corresponding *S*-substituted thiourea salt) may lead to important methods of estimation and separation of metals.

EXPERIMENTAL

S-methylthiourea sulphate, $CH_3S.C(:NH).NH_2, \frac{1}{2}H_2SO_4$ (Arndt *et al.*, *loc. cit.*), was prepared by adding dimethyl sulphate (12.6 g., 1*M*) in several instalments to an ice-cold, concentrated aqueous solution of thiourea (15.2 g., 2 *M*) in a conical flask the mouth of which was quickly closed by an air condenser after each addition. The mixture was then concentrated on a water-bath, allowed to crystallise at room temperature and purified by recrystallisation from water, yield 20 g. (71% of the theoretical). The compound melts at 244° with decomposition.

Nickel methylmercaptide, $Ni(SCH_3)_2$, was obtained as a brown-red precipitate by adding a solution of *S*-methylthiourea sulphate to a hot ammoniacal solution of cobalt-free nickel chloride (*vide infra*). [Found : Ni, 37.90 ; S (by peroxide fusion method), 40.83. $Ni(SCH_3)_2$ requires Ni, 38.39 ; S, 41.95 per cent]. Conversion factor Ni : $Ni(CH_3S)_2 = 0.3839$.

Cuprous methylmercaptide, $Cu(SCH_3)$, was obtained as a yellow precipitate by mixing a solution containing excess of *S*-methylthiourea sulphate to a hot ammoniacal cupric sulphate solution (*vide infra*). [Found : Cu, 51.41 ; S (by peroxide fusion), 28.30. $Cu(SCH_3)$ requires Cu, 57.45 ; S, 28.90 per cent]. Conversion factor Cu : $Cu(SCH_3) = 0.5745$.

Nickel solutions were prepared by dissolving cobalt-free nickel chloride (reagent quality, E. Merk, Darmstadt, approximately 20 g. $NiCl_2, 6H_2O$ per litre), in which nickel was estimated as dimethylglyoximate (Treadwell and Hall, "Analytical chemistry", Vol. II, 1942, p. 193). Copper solutions were prepared by dissolving copper sulphate (extra pure, E. Merck, Darmstadt, approximately 39.4 g. $CuSO_4, 5H_2O$ per litre) in which copper was estimated iodimetrically (*ibid.*, p. 610). Approximately 20.5 g. $ZnSO_4, 7H_2O$ (extra pure, cadmium-free, E. Merk, Darmstadt) in 500 c. c. water was used as the stock solution for zinc, in which zinc was estimated as pyrophosphate (*ibid.*, p. 200). All the above estimations were made in duplicate with exactly concordant results.

In taking any measured volume or in making any titration, the same calibrated standard burette was consistently used throughout the work. All weights recorded are correct up to four significant figures.

Estimation of Nickel

A three-fold excess of the reagent *S*-methylthiourea sulphate (1.2 g. for each 0.1 g. nickel) in minimum quantity of water was added to different measured volumes of the

nickel chloride solutions, each diluted to 20 -250 c.c. The mixture was heated to 80°-90° and an appropriate quantity of liquor ammonia (7·8 c.c. for every g. of the reagent added) was added with vigorous stirring, when a brown-red precipitate of nickel methylmercaptide appeared. The precipitate was allowed to settle at 50°-60° on an asbestos board for half an hour, then filtered through a Gooch crucible (No. 4), washed with warm water and dried at 100° til constant weight. (Drying for about one hour is necessary). Results are shown in Table I. The effect of variation in the amount of liquor ammonia, keeping the amount of nickel (and hence that of the reagent) fixed, is also shown in Table I. The drying temperature was fixed at 100° as the precipitate showed a progressive gain in weight when heated at higher temperatures, presumably due to oxidation. At 100°, the stoichiometric composition was attained in one hour at most and the tendency to gain in weight became perceptible only on heating for more than 100 minutes.

TABLE I

Nickel taken.	Reagent added.	Liq. ammonia added.	Wt. of NH_4Cl.	Wt. of nickel methylmercaptide.	Ni found.	Error.
0.04846 g.	0.6 g.	4.5 c c.	...	0.1262 g	0.04845 g.	−0.01 mg.
0.07269	0.9	7	...	0 1890	0.07256	−0.13
0.09692	1.2	10	...	0.2527	0.09701	+0.09
0.1211	1.4	12	...	0.3164	0.1214	+0.3
0.1453	1.7	15	...	0.3792	0 1455	+0.2
0.1937	2.2	19	...	0.5056	0.1941	+0.4
0.09585	1.2	4	...	0.2427	0.09315	−2.70
0.09585	1.2	5	...	0.2440	0 09371	−2.14
0.09585	1.2	6	...	0.2451	0.09410	−1.75
0.09585	1.2	8	...	0 2496	0.09583	−0 02
0.09585	1.2	10	...	0.2498	0.09590	+0 05
0.09585	1 2	15	...	0.2495	0 09579	−0.06
0 09585	1 5	15—20	1.0 g.	0.2498	0.09590	+0.05
0.09692	1.5	15—20	2 0	0.2528	0 09705	+0.13
0.09585	3.0	30—40	5.0	0.2494	0.09574	−0.11

It is seen that on using 4, 5 or 6 c. c. of liquor ammonia (for 1.2 g. reagent), the results obtained are too low. There appears to be a minimum critical p_H for the complete precipitation of nickel as methylmercaptide. The amount of ammonia should therefore be chosen to be 7·8 c.c. for each gram of the reagent.

Effect of Ammonium Ion.—To solutions of nickel containing different amounts of ammonium chloride (reagent ; E. Merk, Darmstadt), diluted to about 200 c. c. and kept warm at 80°-90°, a four-fold excess of *S*-methylthiourea sulphate (1.5 g. for each 0.1 g. nickel) in concentrated aqueous solution was added in four or five instalments in course of half an hour ; each addition of the reagent was followed by that of 4-5 c.c. liquor ammonia (15-20 c. c. in total) and the mixture stirred vigorously. The complete preci-

pitation is indicated by the disappearance of blue colour in the supernatant liquid. With 5 g. of ammonium chloride, however, 3 g. of the reagent and 30-40 c.c. of liquor ammonia in total are required for the precipitation to be completed.

The mixture was kept warm for another half an hour, and then filtered, washed, dried and weighed as before. The results are shown in Table I.

Estimation of Copper

A concentrated solution of *S*-methylthiourea sulphate (at least 1.5 g. solid reagent for each 0.1 g. copper) was added with stirring to an ammoniacal cupric solution (containing 7 c.c. liquor ammonia for every g. of *S*-methylthiourea sulphate added), diluted to 150-200 c. c. and the mixture kept warm at 80°-90° ; a yellow precipitate of cuprous methylmercaptide appeared. The mixture was warmed at 50°-60° for half an hour, filtered through a Gooch crucible No. 4, washed with warm water and dried to a constant weight at 100°. (Drying for one hour or a little more is sufficient). The results are shown in Table II.

Adopting exactly the above procedure, but using a fixed volume, 5 c. c.. of alkaline tartrate solution * (prepared by mixing equal volumes of 75% Rochelle salt A.R. solution and 24% caustic soda, A.R. solution) in place of varying quantities of liquor ammonia, copper was precipitated as $Cu(SCH_3)$ and weighed as such. The results are shown in Table II.

The washed precipitate of $Cu(SCH_3)$ attained the stoichiometric composition on heating for about an hour at 100°, and on prolonging the heating to a period of two hours or even more, the precipitate kept a constant weight.

TABLE II

Cu taken.	Cu (SCH_3).	Cu found.	Error.	Cu taken.	Cu (SCH_3).	Cu found.	Error.
	Medium :ammonia.				Medium :alkaline tartrate.		
0.1009 g.	0.1758 g.	0.1010 g.	+0.1 mg.	0.1021	0.1782 g.	c.1023 g..	+0 2 mg.
0.1513	0.2628	0.1510	−0.3	0.1532	0 2672	0.1535	+0.3
0.2017	0.3510	0.2017	±0.0	0.2042	0.3562	0.2046	+0.4
0.2598	0.4533	0.2604	+0.6	0.2552	0.4444	0.2554	+0.2

Separation of Copper and Nickel

To a solution containing a mixture of copper sulphate and nickel chloride, not exceeding 50-60 c.c. in volume, an equal volume of 5% ammonium oxalate (Merck, Reagent) solution was added. The mixture was heated to 80°-90° and 10 c.c. of liquor ammonia together with a concentrated solution of *S*-methylthiourea sulphate (1.5 g. for each 0.1 g. Cu) was added with constant stirring. The yellow precipitate of cuprous methylmercaptide formed was filtered out immediately, washed, dried and weighed as before. Nickel was estimated as dimethyl glyoximate from the

* Excess of alkaline tartrate solution should be scrupulously avoided as cuprous methylmercaptide dissolves in strong alkalies like caustic soda.

filtrate. The results are shown in Table III. It is seen that the results for copper found in this way is 0.4-0.7% too high and those for nickel, 0.3-0.5% too low.

If the yellow precipitate of cuprous methylmercaptide first formed is allowed to stand in contact with the parent liquid, it gradually turns brownish due to the more and more contamination of nickel methylmercaptide; the single precipitation method cannot therefore be relied upon, particularly, because of uncertainty of the time taken in filtration.

Good results were, however, obtained by the double precipitation method; the precipitate first formed, after being immediately filtered through a quantitative filter paper, was dissolved and transferred to a beaker using 20 c.c. of concentrated hydrochloric acid and minimum quantity of water and kept at 80°-90° for half an hour to drive off the methylmercaptide formed. The solution was then cooled and after adding 50-60 c.c. of 5% ammonium oxalate solution was neutralised by ammonia. Then 10 c. c. of liquor ammonia and 1.5 g. of the reagent for each 0.1 g. of copper were added, and the procedure described previously was followed for the estimation of copper. The first and second filtrates were mixed together and nickel was estimated therefrom by dimethylglyoxime. The results are shown in Table III.

TABLE III

† Cu taken.	‡ Ni taken.	Cu found.	Error.	Ni found in the filtrate.	Error.
		Single precipitation.			
0.1021 g.	0.04793 g.	*0.1028 g.	+0.7 mg.	0.04768 g.	−0.25 mg.
0.1532	0.07190	*0.1539	+0.7	0.07169	−0.21
0.0993	0.09924	**0.1042	+4.9	0.09545	−3.79
		Double precipitation.			
0.04765	0.09924	0.04964	−0.01	0.09915	−0.09
0.09930	0.09924	0.09938	+0.08	0.09915	−0.09
0.04965	0.1240	0.04958	−0.07	0.1246	+0.06
0.1986	0.02481	0.1985	−0.1	0.02489	+0.08
0.1986	0.04962	0.1984	−0.2	0.04963	+0.01
0.2481	0.02481	0.2481	±0.0	0.02468	−0.13

† As estimated individually by iodimetry.
‡ As estimated individually as dimethyl glyoximate.
* Filtering $Cu(SCH_3)$ immediately after precipitation.
** Filtering $Cu(SCH_3)$ after half an hour from the time of precipitation.

Separation of Copper and Zinc

Copper was estimated as cuprous methylmercaptide from a solution containing copper and zinc sulphates, adopting the same procedure as in the individual determination of copper using ammonia medium. The result showed a 4.1% higher value for copper, indicating that co-precipitation of zinc had taken place (Table IV). If the first precipitate of cuprous methylmercaptide were dissolved in 20 c.c. of concentrated hydrochloric acid and a little water and reprecipitated, following the same procedure,

the result was yet 0.9% too high (Table IV). Again, single precipitation by the usual method after adding 1.5 to 2 g. of ammonium chloride for each 100 c.c. of the solution, gave the result 3.3% too high (Table IV). It was therefore thought desirable to dissolve the cuprous methylmercaptide, thus obtained, in concentrated hydrochloric acid and reprecipitate it as before after the addition of 1.5 to 2 g. of ammonium chloride per 100 c.c. of the solution; from the mixture of filtrates obtained from the two successive precipitations, zinc was estimated as pyrophosphate. The results were found satisfactory for both copper and zinc (vide Table IV).

TABLE IV

*Cu taken.	**Zn taken.	Cu found.	Error.	Zinc found.	Error.	Method
0.1985 g.	0.2083 g.	0.2068 g.	+8.2 mg.	...	...	Single precipitation with ammonia only.
0.1986	0.2083	0.2004	+1.8	...	...	Double precipitation with ammonia only.
0.1986	0.2083	0.2051	+6.5	...	...	Single precipitation in presence of NH_4Cl
0.1986	0.2083	0.1982	−0.4	0.2080 g.	−0 3 mg.	Double precipitation in presence of NH_4Cl.
0.1986	0.05208	0.1982	−0.4	0.05211	+0.03	"

* As estimated individually by iodimetry.
** As estimated individully as pyrophosphate.

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SULPHONAMIDE DERIVATIVES OF THIAZOLES. PART I

By Bhaskar Das and M. K. Rout

Six different 2-acetylaminothiazoles have been condensed with chlorosulphonic acid, and the resulting 5-sulphonyl chloride derivatives have been converted into the corresponding 2-amino-5-sulphonamides and 5-substituted sulphonamides. These aminothiazoles have also been condensed with acetylsulphanilyl chloride, *p*-fluorobenzenesulphonyl chloride and *p*-xylenesulphonyl chloride with a view to ascertaining the effect produced by replacement of NH_2 group by F atom and alkyl group.

Investigations for the synthesis of compounds related to sulphanilamide and for the study of their chemotherapeutic properties with a view to overcoming some of the drawbacks of the drugs so far known (Goodman and Levy, *J. Amer. Med. Assoc.*, 1937, **109**, 1005; Bucy, *ibid.*, 1937, **109**, 1007) comprised mainly replacement of the amido-H by some other group or chain, mostly heterocyclic residues, since these led to the discovery of sulphathiazole, sulphadiazine and sulphaguanidine. That such replacements are expected to have great therapeutic importance has also been stressed by several workers (Whiteley, *Lancet*, 1937, *i*, 1517 ; Crossby *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 2217). Though some compounds possessing thiazolyl residues at N^1 have been prepared, systematic study involving variation of substituents on the thiazolyl nucleus does not seem to have been undertaken. It is the object of the present investigation to fill up some of these gaps. The amino group in the resulting thiazoles has also been replaced by F atom and alkyl group to evaluate the effect of such variations, these replacements being accomplished by substituting *p*-fluorobenzenesulphonyl chloride and *p*-xylenesulphonyl chloride for acetylsulphanilyl chloride in the reaction with 2-aminothiazoles.

Since the curative effect of sulphanilamide has been attributed to the presence of a sulphonamide group ($SO_2.NH_2$) and an NH_2 group in *para* position to it on the phenyl necleus, it is considered of interest also to study the effect of the fixation of these groups on the thiazole nucleus. With this object in view, several 2-amino-5-sulphonamidothiazoles have been prepared. Reference may be made in this connection to the observation that sulphur in cyclic union is the equivalent of $-CH=CH-$ group, as is well illustrated in the close parallelism in physical and chemical properties between the benzene and the thiophene series or between thiazoles and the corresponding pyridines. These resulting thiazolylsulphonamides therefore carry the amino group in a position which is to all intents and purposes *para* to the sulphonamide group.

Six different thiazoles have now been prepared by following the method of Rout and Pujari (*J. Amer. Chem. Soc.*, 1953, **75**, 4057). These and their acetyl derivatives are described in Table I. The preparation of one of these compounds is illustrated in the Experimental.

These 2-acetylaminothiazoles have been converted into the corresponding 5-thiazolesulphonyl chlorides by treatment with chlorosulphonic acid. The resulting sulphonyl

chlorides were then condensed with NH_3 and aniline, and the products formed were subsequently hydrolysed to obtain the corresponding 2-amino-5-sulphonamides and 5-phenylsulphonamides. The experimental procedure employed for the above condensations are described in the Experimental. The properties, m. p. and analytical data of these compounds are described in Table II.

The sulphonyl chloride compound, derived from 4-phenyl-2-acetylaminothiazole, has also been condensed with nine different amines, and the resulting 2-acetamidosulphonamides have been hydrolysed to the corresponding 2-aminosulphonamides. Table III records the analytical data, m. p. etc. of the above products.

The 2-aminothiazoles, prepared above, have also been condensed with acetylsulphanilyl chloride, *p*-fluorobenzenesulphonyl chloride and *p*-xylenesulphonyl chloride. The 2-acetamidosulphonamides have also been hydrolysed to the corresponding 2-amino compounds. The methods of preparation of these compounds are illustrated in the Experimental and their analytical data are described in Tables IV and V.

Testing of bactericidal properties of these compounds is in progress.

EXPERIMENTAL

4-p-*Tolyl*-2-*aminothiazole* (I) was prepared by our modified method (*loc. cit.*) by the reaction of *p*-methylacetophenone (6.7 g.) with thiourea (7.6 g.) and iodine (12.7 g.). The base was purified by recrystallisation from alcohol, m. p. 127°, yield 85%. (Found: S, 16.50. $C_{10}H_{10}N_2S$ requires S, 16.84 per cent). Other 2-aminothiazoles have also been prepared in the above manner.

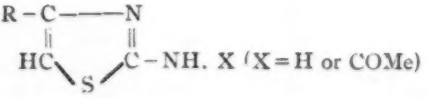
2-*Acetamino*-4-p-*tolylthiazole* (II).—The compound (I, 6 g.) was refluxed with acetic anhydride (15-20 c. c.) for about one hour, cooled and poured into water. The precipitate obtained was filtered and crystallised from alcohol, m. p. 204°, yield 95%. (Found: S, 13.88. $C_{12}H_{12}ON_2S$ requires S, 13.80 per cent).

4-p-*Tolyl*-2-*acetamino*-5-*thiazolesulphonyl Chloride* (III).—In a dry flask, chlorosulphonic acid (15.25 g.) was taken and cooled to 10°-15° in a water-bath containing a few pieces of ice, and to it finely powdered dry compound (II, 6.1 g.) was added in small portions and with good mixing so that the temperature did not rise above 20°. After the compound had dissolved, the flask was heated at 100° for 3 hours after which the content was poured slowly into a well-stirred mixture of 140 g. of finely cracked ice and enough water to make the stirring easy. The precipitate was filtered, washed several times with ice-cold water and dried in a vacuum desiccator over NaOH. An elemental analysis showed the presence of chlorine in the compound which was crystallised from acetone, m. p. 210° (decomp.), yield 60%. (Found: Cl, 10.25; S, 18.92. $C_{12}H_{11}O_3N_2ClS_2$ requires Cl, 10.74; S, 19.36 per cent).

4-p-*Tolyl*-2-*acetamino*-5-*thiazolesulphonamide* (IV).— To the compound (III) (1 g.), nearly 3 c. c. of concentrated NH_4OH was added and the mixture was rubbed by a glass rod to a smooth thin paste. The mixture was then refluxed on a water-bath at 70° for 1 hour. After cooling the mixture in ice-bath, it was acidified with H_2SO_4 (dil.) until acid to Congo red. After thorough chilling in the ice-bath, the precipitate was filtered, washed with ice-cold water and crystallised from dilute alcohol, m.p. 271° (decomp.), yield 25%. (Found: S, 21.02. $C_{12}H_{12}O_3N_3S_2$ requires S, 20.57 per cent).

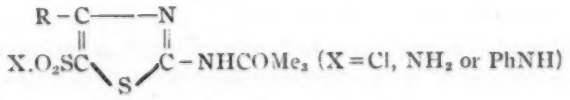
4-Phenyl-2-amino-5-thiazolesulphonamide (V).—To 4-phenyl analogue of (IV) (1g.) nearly 3 to 4 c. c. of 12% HCl was added and the mixture was refluxed for 2 hours, and it was then poured into a beaker, diluted with equal volume of water, heated to boiling and filtered. To the filtrate solid Na_2CO_3 was added in small portions with continuous stirring until the solution was just alkaline to litmus. The precipitate formed was filtered, washed with cold water and recrystallised from alcohol, m. p. 265° (decomp.), yield 40%. (Found: S, 25.32. $C_9H_9O_2N_3S_2$ requires S, 25.09 per cent).

TABLE I



Nature of substituent R.	2-Amino 4-arylthiazole.				Acetyl derivative			
	M.P.	Yield.	% Sulphur Found.	% Sulphur Calc.	M.P	Yield.	% Sulphur, Found.	% Sulphur, Calc.
1. Phenyl	151°	85%	18.68	18.18	205°	90%	15.03	14.63
2 *p*-Tolyl	127°	85	16.50	16.84	204°	95	13.88	13.80
3 *p*-Chlorophenyl	163°	70	14.82	15.20	258°	90	12.15	12.67
4. *p*-Methoxyphenyl	184°	80	14.75	15.58	176°	80	13.45	12.90
5. *p*-Ethoxyphenyl	242°	80	14.93	14.54	...	...	...	...
6. *p*-Methoxyphenylvinyl	128°	60	14.48	13.80	...	...	...	...

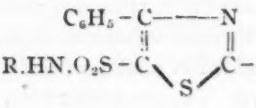
TABLE II



Nature of substituent R.	2-Acetylamino-4-aryl-5-thiazolesulphonyl chloride (X=Cl).						Corresponding sulphonamide (X=NH_2).				Corresponding phenylsulphonamide (X=PhNH).			
	M.P	Yield.	% Sulphur. Found.	% Sulphur. Calc.	% Chlorine. Found.	% Chlorine. Calc.	M.P.	Yield	% Sulphur Found.	% Sulphur Calc.	M.P.	Yield.	%Sulphur. Found	%Sulphur Calc.
1. Phenyl	*214°	80%	20.64	20 22	10 85	11.21	*285°	30%	21.96	21.53	*275°	70%	17.55	17.15
2. *p*-Tolyl	*210°	60	18.92	19 36	10.25	10.74	*271°	25	21.02	20.57	*219°	50	17.10	16.53
3. *p*-Chlorophenyl	*200°	65	18 88	18.23	19.80	20 22	205°	20	19.98	19.30	127°	35	15.28	15.70

* Melts with decomposition.

TABLE III



Nature of substituent R.	4-Phenyl-2-acetamino-5-arylsulphonamidothiazole (X=COMe).				4-Phenyl 2-amino-5-arylsulphonamidothiazole (X=H).		
	Yield.	M.P.*	% Sulphur		M.P.*	% Sulphur.	
			Found.	Calc.		Found.	Calc.
1. Phenyl	70%	275°	17.55	17.15	224°	19.08	19.33
2. *o*-Tolyl	65	268°	16.48	16.53	188°	18.02	18.55
3. *m*-Tolyl	60	248°	16.92	16.53	115°	18.78	18.55
4. *p*-Tolyl	70	250°	16.15	16.53	218°	18.25	18.55
5. *o*-Chlorophenyl	50	220°	15.77	15.71	160°	17.02	17.48
6. *m*-Chlorophenyl	45	241°	15.62	15.71	178°	17.53	17.48
7. *p*-Chlorophenyl	50	259°	15.55	15.71	...	...	...
8. α-Naphthyl	45	286°	15.45	15.13	...	...	...
9. β-Naphthyl	45	263°	15.82	15.13	...	...	...

* All the compounds melted with decomposition.

4-p-*Tolyl-2-acetamino-5-phenylsulphonamidothiazole* (VI).—In a dry conical flask, aniline (0.31 g.) and compound (III, 1.1 g.) were taken and to that 10 c. c. of dry pyridine was added. The mixture was refluxed on a water-bath at 65°-70° for 2½ hours. After heating, the mixture was cooled and diluted with water when a precipitate appeared. It was filtered, washed thoroughly with water, and recrystallised from alcohol, m. p. 219° (decomp.), yield 50%. (Found: N, 11.25; S, 17.10. $C_{18}H_{17}O_3N_3S_2$ requires N, 10.85; S, 16.53 per cent).

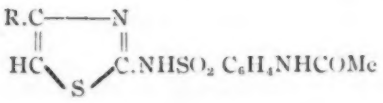
4-*Phenyl-2-amino-5-phenylsulphonamidothiazole* (VII).—The 4-phenyl-2-acetamino-5-phenylsulphonamidothiazole was hydrolysed to the corresponding 2-amino compound in the manner described earlier, m. p. 223° (decomp.), yield 60%. (Found: S, 19.08. $C_{15}H_{13}O_2N_3S_2$ requires S, 19.33 per cent).

Condensation of 4-p-*tolyl-2-aminothiazole with* p-*Acetamidobenzenesulphonyl Chloride*: 4-p-*Tolyl*-2-(N^4-*acetylsulphanilamido*)*thiazole* (VIII).—4-*p*-Tolyl-2-aminothiazole (0.95 g.) and *p*-acetamidobenzenesulphonyl chloride (1.17 g.) were taken in a dry conical flask and to it 10 c.c. of pyridine was added. The mixture was refluxed on a water-bath at 65°-70° for 2½ hours. After cooling, the mixture was diluted with water when a precipitate appeared. It was filtered, washed thoroughly with water, crystallised from alcohol and dried, m.p. 168-70°, yield 65%. (Found: N, 10.32; S, 16.42. $C_{18}H_{17}O_3N_3S_2$ requires N, 10.85; S, 16.53 per cent).

The above product has also been hydrolysed to the corresponding amino compound, *e.g.*, 4-*p*-tolyl-2-sulphanilamidothiazole, in the manner described earlier, m. p. 124° (decomp.), yield 50%. (Found: N, 12.38. $C_{16}H_{15}O_2N_3S_2$ requires N, 12.17 per cent).

The yields, melting points and analytical data for condensation products of *p*-acetamidobenzenesulphonyl chloride with other 2-aminothiazoles and thier corresponding amino compounds obtained on hydrolysis are shown in Table IV.

TABLE IV



Nature of substituent R	4-Aryl-2-(N¹-acetylsulphanilamido)-thiazole.				4-Aryl-2-sulphanilamidothiazole.			
	Yield.	M.P.	% Nitrogen. Found.	Calc.	Yield.	*M.P.	% Nitrogen. Found.	Calc.
1. Phenyl	70%	124°	11 55	11 26	55%	144-155°	12.50	12.69
2. *p*-Tolyl	65	168-70°	10.32	10.85	65	124°	12 38	12.17
3. *p*-Chlorophenyl	75	155°	10.82	10 31	50	144°	11.92	11.49
4. *p*-Methoxyphenyl	70	*174-76°	9 95	10 42	50	196°	11.55	11 63
5. *p*-Ethoxyphenyl	80	*236°	10 68	10.07	55	210°	11.38	11.20
6. *p*-Methoxyphenylvinyl	55	*185-90°	10.25	9.79	40	195°	11.20	10.85

* Melts with decomposition.

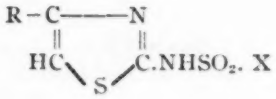
Condensation of 4-p-*Tolyl*-2-*aminothiazole with* p-*Fluorobenzenesulphonyl Chloride* (IX).—Compound (I, 1. g.) and *p*-fluorobenzenesulphonyl chloride (1g.) were heated under reflux with 10 c. c. of pyridine on a water-bath at 65°-70° for 2½ hours. After cooling, the mixture was diluted with water when a gummy product appeared. The supernatant solution was decanted off and the gummy product was dissolved in concentrated NH_4OH and reprecipitated by adding very diluted HCl when a crystalline precipitate was obtained. This was filtered and recrystallised from alcohol, m. p. 108°, yield 85%. (Found: N, 8.42 ; S, 18.82. $C_{16}H_{13}O_2N_2FS_2$ requires N, 8.05 ; S, 18.39 per cent).

Condensation of 4-p-*Tolyl*-2-*aminothiazole with* p-*Xylenesulphonyl Chloride* (X).—Compound (I, 0.95 g.) and *p*-xylenesulphonyl chloride (1.03 g.) were heated under reflux with 10 c. c. of pyridine on the water-bath at 65°-70° for 2½ hours. After cooling, the mixture was poured into water when a semisolid product was obtained. It solidified on standing overnight. It was then filtered and crystallised from alcohol, m. p. 170-75°, yield 70%. (Found: N, 7.80. S, 17.72. $C_{18}H_{16}O_2N_2S_2$ requires N, 7.82; S, 17.87 per cent).

The yields, melting points and analytical data for condensation products of *p*-xylenesulphonyl chloride and *p*-fluorobenzenesulphonyl chloride with other 2-aminothiazoles are shown in Table V.

TABLE V

Condensation products of p-fluorobezenesulphonyl chloride and p-xylenesulphonyl chloride with 2-aminothiazoles.



Nature of R.	X = C_6H_4F Yield.	M.P.	% Nitrogen. Found.	Calc.	X = $C_6H_4(CH_3)_2$ Yield.	M.P.	% Nitrogen. Found.	Calc.
1. Phenyl	55%	148-150°	8.03	8.38	80%	204°	8.22	8.14
2. *p*-Tolyl	85	108°	8.42	8.05	70	170-75°	7.80	7.82
3. *p*-Chlorophenyl	65	*215°	7.98	7.59	55	95-98°	6.85	7.39
4. *p*-Methoxyphenyl	Gummy product				75	*100°	6.88	7.49
5. *p*-Ethoxyphenyl	75	*173°	7.38	7.40	60	*174-76°	7.62	7.21
6. *p*-Methoxyphenylvinyl	50	168-70°	7.82	7.18	50	*120°	7.53	7.00

* Melts with decomposition.

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CHEMICAL EXAMINATION OF THE JUICE OF *CITRULLUS COLOCYNTHIS*. PART I

By Rafat Husain Siddiqui, Iqbal Rafat Siddiqui and Sultan Muhammad

From the juice of bitter apples α-elaterin, citrulluin, citrulluen and citrulluic acid have been isolated.

Citrullus colocynthis or bitter apple (N.O. Cucorbitaceae), locally known as *Tumma or Hinzel*, is widely distributed in the Punjab and Sind and thrives well in arid and sandy soils. Its fruits are bitter in taste with drastic purgative properties and are recognised in the British and the United States pharmacopoeas and find application in cases of billiousness, constipation, fever and intestinal parasites. The juice of the fruit, mixed with sugar, is a household remedy in dropsy. The oil from the seeds is used for snake-bite, scorpion-stings, epilepsy and for the growth and blackening of hair. The root is used in ascites, jaundice, rheumatism and various urinary diseases, especially in amenorrhoea (K. L. Dey, "Indigenous Drugs of India", 1933, p. 121 ; Die Pflanzenstoffe, 1931, p 1196). In some parts of the Punjab bitter apples are used for making pickles (achaar) and as a remedy in bowel complaints of horses.

Walz (*Jahrb. Pharm.*, 1858, **9**, 16, 225 ; 1861, **16**, 10) reported the presence of a yellow amorphous glucoside, colocynthin, and a tasteless crystalline substance, colocynthetin. Henke (*Arch. Pharm.*, 1883, **221**, 200) also obtained colocynthin but could not confirm its glucosidic character. Johannson (*Z. Chem.*, 1885, **24**, 154) isolated colocynthin, α-elaterin etc., while Naylor and Chappel (*Pharm. J.*, 1907, **79**, 99) obtained colocynthin in pale yellow needles. According to Power and Moore (*J. Chem. Soc.*, 1910, **97**, 99) colocynthin and colocynthein are not definite individuals. They isolated citrullol, an amorphous alkaloid, α-elaterin, hentriacontane, an essential oil and a phytosterol. Agarwal and Dutt (*Curr. Sci.*, 1934, **3**, 250) from the roots of the plant obtained hentriacontane, α-elaterin and saponins. Alimchandani, Badami and Tummin Katti (this *Journal*, 1949, **26**, 515) examined the oil from the seeds as well as the matter obtained from the seeds by extracting them with alcohol, petroleum ether, ether and chloroform, and reported a number of products.

The importance of colocynthis in medicine led the authors to examine fresh juice and pulp of the fruits. As a result of this examination the following products were isolated which showed absence of nitrogen and gave colour reactions with concentrated sulphuric acid and did not respond to phenolic and aldehydic tests nor indicated the presence of a methoxyl group :

(*a*) α-Elaterin ($C_{22}H_{28}O_6$, m.p. 233°), a white substance in prismatic needles, which agreed in properties with α-elaterin reported by previous investigators.

(*b*) Citrulluin ($C_{21}H_{30}O_7$), a brown, bitter, neutral, semi-crystalline powder, m.p. 125-27°.

(*c*) Citrulluene ($C_{21}H_{32}O_{10}$), a hydrochloric acid- and water- soluble microcrystalline powder, m.p. 175-78°.

(*d*) Citrulluic acid, bitter yellowish unsaturated acid in prismatic needles, m.p. 109°.

EXPERIMENTAL

The fresh fruits (bitter apples) used in this investigation were obtained from Chistian (Bhawalpur State) and Lyallpur and varied in colour and size. The unripe fruits were green, while the mature and the ripe ones were marbled green with white and yellowish patches. The weight of fresh fruits ranged from half ounce to eight ounces and contained spongy and juicy pulp embedded with seeds. The pulp on drying turned yellowish hard mass. The fruits with weights ranging from 14 to 116 g. yielded pulp 48-60%, rind 17-26% and seeds 4-10% on the weight of fresh fruits. On an average the yield of the dried pulp was 12-15%.

Rind.—The shade-dried, finely powdered rind was extracted with different solvents after taking fresh material each time (Table I,A), and the same material was extracted with petroleum ether, ether, benzene, $CHCl_3$, ethyl acetate, acetone and alcohol in succession (B). The total extracted matter (16.04%) corresponds with that obtained from alcohol (16.6%) as shown in the table (A).

TABLE I

Solvent.	Extracted matter from rind (A).	rind (B).	seeds.	Nature of the extracted matter.
Benzene	2.42%	1.28%	...	Dark green in colour and emits smell of rind.
Acetone	3.21	2.47	...	Dark green with reddish tinge and gives smell of rind.
Ether	2.20	0.44	...	Green.
Chlorofrom	2.88	0.81	...	Yellowish green.
Alcohol	16.60	3.70	2.1	Dark, bitrer ; emits smell of rind.
Ethyl acetate	6.04	3 47	...	Dark and emits smell of rind.
Petroleum ether	3 87	3.87	19.2	Yellowish and greasy.
	Total	16.04	21.03	

Fruits.—The fruits (44 lbs.) were collected and washed with water to remove surface dirt and the extraction of the juice was carried out by spindling. The spindle or *burris* slowly reamed out the pulp from the peel. Immediately after reaming, the juice and pulp were screened to remove seeds and coarse pulp. The pulp and seeds were washed with a little water which was added to the juice. During spindling it was noticed that the fruits produced a considerable quantity of foam and froth. The fruits on burring yielded 45% pulp, 39% rind and 10% seeds. The fine pulp and juice (20 lbs.) were kept in carboys with alcohol (2 litres) and when a clear solution was formed, it was syphoned off and the residual pulp was kept with fresh alcohol (2 litres). After keeping for two days at room temperature the alcoholic extract was removed, and after combining with the main fraction it was filtered. The lemon-yellow filtrate on keeping at room temperature deposited α-elaterin as a white crystalline mass (*a*, 1.2 g.). The mother-liquor was evaporated in vacuum and the insoluble residue in ether and petroleum ether was extracted with ethyl acetate. The ethyl acetate extract, after washing successively

with dilute Na_2CO_3 solution, dilute HCl and water, was dried over anhydrous sodium sulphate, and on removal of the solvent it gave a substance with a peculiar smell which on rubbing with petroleum ether turned into a microcrystalline powder (0.8 g.). It is named as "citrulluin".

The extract, soluble in dilute HCl, was basified with Na_2CO_3 solution and it was again extracted with ethyl acetate, dried over anhydrous sodium sulphate solvent removed, and the residue was dissolved in water. The aqueous extract was evaporated to dryness and on rubbing with petroleum ether gave citrulluene as a brittle powder (*c*).

The extract, soluble in Na_2CO_3, on acidification with dilute HCl was extracted with ethyl acetate. After removal of the solvent a residue was obtained which on rubbing with petroleum ether yielded citrulluic acid as a yellowish powder (*d*).

The mother-liquors from the above fractions will be examined later.

Fraction (a) : *α-Elaterin.*—On recrystallisation from ethyl acetate it was obtained in white glistening prisms which turned yellow at 220° and melted at 233°. It is tasteless, neutral in reaction and is soluble in benzene, ethyl acetate, chloroform, sparingly so in acetone and alcohol, and insoluble in petroleum ether, water, dilute acids and alkalies. It does not decolorise bromine in CCl_4 nor responds to any test for aldehydic and phenolic groups. It dissolvesin warm concentrated nitric acid with a straw colour and turns orange-red in contact with H_2SO_4 (conc.), and finally produces a deep orange-red solution which with a crystal of potassium chlorate and dichromate turns bright yellow and light yellowish green respectively. There was no loss in weight on drying. [Found (undried) : C, 68.03 ; H, 7.72. Found (dried at 120°) : C, 68.05 ; H, 7.90 ; OMe, 5.98 ; M. W., 385. $C_{22}H_{28}O_6$ requires C, 68.04 ; H, 7.73; OMe, 7.9 per cent. M.W. 388]. The following formulae, suggested by Power and Moore for the substance, do not agree with our analytical data.

TABLE II

Formula.	Calc.	Found by	
		Power & Moore.	present authors.
$C_{20}H_{28}O_5$	C : 68.9	68.9	68.03, 68.23
	H : 8.0	8.1	7.72, 7.90
$C_{24}H_{34}O_6$	C : 68.9		
	H : 8.0		
$C_{28}H_{38}O_7$	C : 69.1		
	H : 7.8		

Fraction (b).—Citrulluin was obtained as a microcrystalline powder, m. p. 125-27°. It is bitter in taste, neutral in reaction and is soluble in acetone, alcohol, chloroform, ethyl acetate, and insoluble in ether, petroleum ether and water. It dissolves in H_2SO_4 (conc.) to a deep red solution and the colour disappears on dilution, but on adding a crystal of potassium chlorate or dichromate it turns yellow. It suffered no loss on drying. [Found (dried at 120°) : C, 63.97 ; H, 7.60 ; OMe, 5.12 ; M. W., 375, 382 (partly soluble in camphor). $C_{21}H_{30}O_7$ requires C, 63.96 ; H, 7.61 ; OMe, 7.85 per cent. M.W., 394].

Fraction (c).—Citrulluene was obtained as a microcrystalline powder, m. p. 175-78° which showed absence of nitrogen. It is soluble in water, alcohol, ethyl acetate, chloroform and acetone, and insoluble in ether and petroleum ether. It dissolves in HNO_3 (conc.) to a yellow solution on warming and the behaviour with H_2SO_4 is the same as with citrulluin. It suffered no loss in weight on drying at 120°. [Found : C, 56.75, 56.73 ; H, 7.38, 7.2 ; OMe, 4.37; M. W. 418 (substance partly soluble in camphor). $C_{21}H_{32}O_{10}$ requires C, 56.75 ; H, 7.20 ; OMe, 6.98 per cent. M. W., 444].

Fraction (d).—Citrulluic acid, on recrystallisation from ether-petroleum ether mixture in yellowish prismatic needles, had m. p. 109° (Alimchandani *et al.*, *loc. cit.*, record m. p. 112°). It is soluble in ethyl alcohol, chloroform, acetone and benzene, but insoluble in water and dilute acids. It evolved carbon dioxide on treatment with sodium bicarbonate solution and decolorised bromine in CCl_4 and acid and alkaline $KMnO_4$ solutions. Its behaviour with sulphuric acid is the same as with citrulluin and citrulluene.

This work, at present, has been suspended owing to the departure from the College of two associates. The analyses reported in this investigation were done by Dr. G. Weiller and Dr. F. D. Strauss (Oxford).

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PHYSICO-CHEMICAL STUDIES ON THE COMPLEX FORMATION BETWEEN THORIUM ION AND OXALATE ION. PART II. THERMOMETRIC AND CRYOSCOPIC TITRATIONS

By Monisha Bose and D. M. Chowdhury

The existence of different thoro-oxalates in solution has been corroborated by thermometric and cryoscopic titrations with thorium nitrate-potassium oxalate systems.

The dissolution of thorium oxalate in excess of ammonium oxalate (*Bahr. Annalen*, 1864, **132**, 231) is an important reaction from the standpoint of analytical chemistry. Bunsen (*Ann. Phys. Chem.*, 1875, **155**, 375) showed that this behaviour of thorium oxalate distinguished it from the rare-earth oxalates and formed the basis of separation of thorium from rare earths. Brauner (*J.Chem. Soc.*, 1898, **73**, 951) ascribed this specific dissolution to the formation of a double oxalate, and succeeded in isolating a highly soluble compound of the formula, $(NH_4)_4[Th(C_2O_4)_4]$, $4H_2O$; he also found that this substance on hydrolytic decomposition yielded an almost insoluble compound of the formula, $(NN_4)_2[Th_2(C_2O_4)_5]$. Wirth and Hauser (*Z. anorg. Chem.*, 1912, **78**, 75) investigated the solubilities and stability ranges of the different oxalato compounds, and claimed to have isolated with difficulty a third oxalato compound of the composition, $(NH_4)_2[Th(C_2O_4)_3]$, $3H_2O$, which was found to be rather insoluble.

Beyond the isolation of the different oxalato compounds in the solid state and the determination of their solubilities and stability ranges, no thorough or systematic investigation of such compounds from the physico-chemical point of view has yet been made. Literature is silent as to the existence in solution of the different thoro-oxalato complexes. If they are stable in solution, it would be of interest to ascertain in which form do they exist in solution phase. Because, a complex molecule, stable in solid phase, may not be stable in solution phase, and *vice versa*. A complex, stable in solid phase in one form, may exist in solution in a different form. In the present work attempts have been made by thermometry and cryoscopy with thorium nitrate-potassium oxalate system to gain an insight into the nature and conditions of their existence in solution and stability ranges of the different thoro-oxalates.

Experimental

Thermometric Titrations

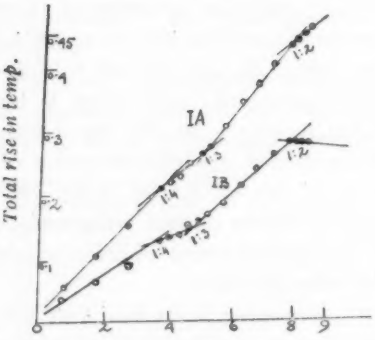
The thermometric titration arrangement was made according to the procedure laid down by Halder (this *Journal*, 1946, **23**, 147). The reagents used were of "Analar" quality. Thorium was estimated as thorium dioxide (ThO_2) and the oxalate solutions were standardised against permanganate.

As the strong solutions of oxalate were required for thermometric titrations, potassium oxalate, being much more soluble than ammonium oxalate, was employed

in the work. In the titrations, thorium nitrate was always added to the oxalate solutions. The reverse process of the addition of potassium oxalate to thorium nitrate solution furnishes another complex of thorium of the nature of $[Th(C_2O_4)]_m^{+2m}$, (unpublished), and then the insoluble thorium oxalate, $[Th(C_2O_4)_2]$, which then transforms in the excess of oxalate of potassium to afford $[Th_2(C_2O_4)_5]^{2-}$ or $[Th(C_2O_4)_3]^{4-}$, and finally dissolves to form $[Th(C_2O_4)_4]^{4-}$. Since the latter process, *i.e.* dissolution of thorium oxalate in potassium oxalate, proceeded at a very slow rate in the cold, this reverse process was not attempted for this system.

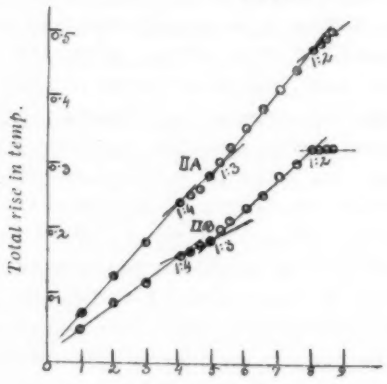
Results of the thermometric titrations of different concentrations of thorium nitrate and potassium oxalate solutions are shown in Figs. 1-3. A correction for the blank

FIG. 1



Curve IA-0.12*M*-$K_2C_2O_4$ + 0.3*M*-$Th(NO_3)_4$ (without corr.)
IB- Do Do (after corr.)

FIG. 2



IIA-0.13*M*-K_2Cr_2O + 0.325*M*-$Th(NO_3)_4$ (without corr.)
IIB- Do Do (after corr.)

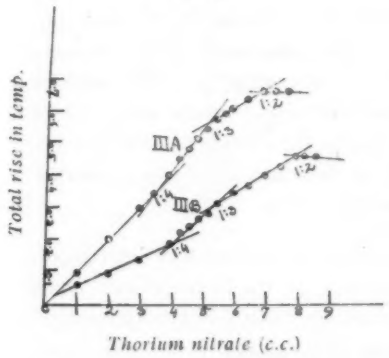
has been applied. For, when one adds thorium nitrate solution to potassium oxalate solution, there are two simultaneous processes, viz. (*i*) dilution of thorium nitrate, and (*ii*) reaction between thorium nitrate and potassium oxalate. Evidently, the heat of reaction for the successive additions of thorium nitrate to potassium oxalate solution will be different from that if there were no heat-change due to the dilution of thorium nitrate. So, it was necessary to make blank-correction. This was done by running parallel titrations for each different strength of thorium nitrate solutions and using water in place of potassium oxalate solutions of corresponding strengths, and then by subtracting the heat-changes for each successive addition of thorium nitrate to water from the corresponding heat-changes for each similar successive addition of the same thorium nitrate solution to potassium oxalate solution of its corresponding strength. This heat-change is proportional to temperature-difference, and so, only temperature-differences have been plotted against the titre values. The application of the blank-correction factor shows that, if there be made no blank-correction, the heat-change goes on increasing even after the completion of the reaction at $[Th^{4+}]:[C_2O_4^{2-}] = 1:2$, which is evident from the upward rise of the curves (curves IA

and IIB in Figs. 1 and 2) after (1 : 2). But when blank-correction is made, there is no heat-change after (1 : 2), which can be seen from the horizontal parts of the curves IB and IIB,IIIA and IIIB (Figs. 1-3).

All the thermometric curves show sharp changes in their slopes corresponding to $[Th^{4+}] : [C_2O_4^{2-}]$ ratios equal to 1 : 4, 1 : 3 and 1 : 2 respectively. The break at $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 2$ indicates the precipitation of highly insoluble normal thorium oxalate, $Th(C_2O_4)_2$, to which the present workers are not interested. The break corresponding to $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 4$ indicates the formation of the complex ion, $[Th(C_2O_4)_4]^{4-}$. Another break corresponding to $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 3$ appears too. It is due to the formation of $[Th(C_2O_4)_3]^{2-}$ ion.

From the curves it can be said that the existence of the complex ion, $[Th(C_2O_4)_4]^{4-}$ is indicated at all concentration regions. The break at $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 4$ in the curves for dilute regions are not very sharp, and the system being a complicated one, the rise in temperature is not so high. Still one can be sure of the existence of the complex ion, $[Th(C_2O_4)_4]^{4-}$, in solution phase. The breaks at $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 4$ appear more pronounced and well defined and sharp in concentrated regions, and the thorium-oxalato complex due to the dissolution of thorium oxalate in alkali oxalate exists definitely in solution phase as anionic thorium-tetraoxalato complex, $[Th(C_2O_4)_4]^{4-}$, which is the main point of investigation.

FIG. 3



IIIA-0·423*M*-$K_2C_2O_4$ and 1·135*M*-$Th(NO_3)_4$ after blank correction.
IIIB-0·2*M*-$K_2C_2O_4$ and 0·5*M*-$Th(NO_3)_4$ after blank correction

The break at $[Th^{4+}] : [C_2O_4^{2-}] = 1 : 3$ is probably due to the formation of another complex ion, $[Th(C_2O_4)_3]^{2-}$, and as there is no break found in the region $[Th^{4+}] : [C_2O_4^{2-}] = 2 : 5$, it may be concluded that the Brauner's compound, $[Th_2(C_2O_4)_5]^{2-}$, is a double compound of $[Th(C_2O_4)_3]^{2-}$ and $Th(C_2O_4)_2$ in the solid phase.

Cryoscopic Titration

Löwenhartz (*Z. physikal. Chem.*, 1895, **18**, 70) first showed that Raoult's law of cryoscopic lowering was applicable to the lowering of the transition point of a salt-hydrate, e.g., the transition of $Na_2SO_4 - Na_2SO_4, 10H_2O$ in presence of their saturated solution. More recently, Müller (*Anal. chim.*, 1937, **7**, 8) has shown that this property of cryoscopic lowering can also be applied in eutectic systems (ice and one or more salt) and this offers several advantages over classical cryoscopy in aqueous medium, in as much as, (*i*) the activity coefficient of the added substance is almost constant with variation in concentration, as the ionic strength of the medium, being already very

high, remains practically unaffected, and (*ii*) cryoscopic lowering is not affected by ions in common with the cryoscopic medium.

The molecular lowering being a colligative property, depends on the number of ions in solution. Thus, when thorium nitrate is gradually added in small amounts to potassium oxalate in KNO_3, used as the cryoscopic medium, the cryoscopic lowering will gradually change due to the removal of the free oxalate ions by complex formation or precipitation, and breaks will appear in the cryoscopic lowering-titre curves, corresponding to the ends of certain reactions.

The apparatus consists of a freezing bath provided with a wooden lid carrying two holes. Through the central hole passes a wide test tube, held in position by a tightly fitting cork. Through the second hole a stirrer is introduced for stirring the freezing bath. Within the wider tube, a smaller test tube containing the eutectic mixture is fitted tightly by a rubber ring. The smaller test tube is provided with a cork having three holes, one for inserting a Beckmann differential thermometer, another for a stirrer and a third for adding the titre. The temperature of the freezing bath is never allowed to fall 3° below the freezing point of the eutectic. The solution may become supercooled but the supercooling is never allowed to exceed half a degree below the normal freezing point. Vigorous stirring initiates the process of solidification, and temperature remains constant during this change of state for nearly 3 to 4 minutes, thereby eliminating the necessity of determining the cooling curve.

First, the eutectic temperature of the potassium nitrate-ice system was determined. For this 50 c.c. of 12% KNO_3 was used and the temperature of its freezing was noted on the Beckmann thermometer. Next 50 c.c. of potassium oxalate of known strength in 12% KNO_3 solution was taken in the inner tube and the freezing point was determined as above and the freezing temperature was read from the thermometer. From the actual lowering, the molecular lowering due to potassium oxalate was calculated and compared with the standard known value of the molecular lowering. This process serves also to calibrate the Beckmann thermometer. Then to this potassium oxalate solution in potassium nitrate, thorium nitrate was added in small portions and the freezing point was determined as usual. Molecular lowering, or freezing point depression, or the freezing points for successive additions of thorium nitrate to $K_2C_2O_4 - KNO_3$ system may be plotted against the titre values. Here the last-named process was followed, *i.e.* the freezing points as read on the Beckmann thermometer for different successive additions of thorium nitrate to potassium oxalate in potassium nitrate solution were plotted against the corresponding titre values, and graphs were obtained. Results of the cryoscopic determinations at different concentrations are shown in Fig. 4.

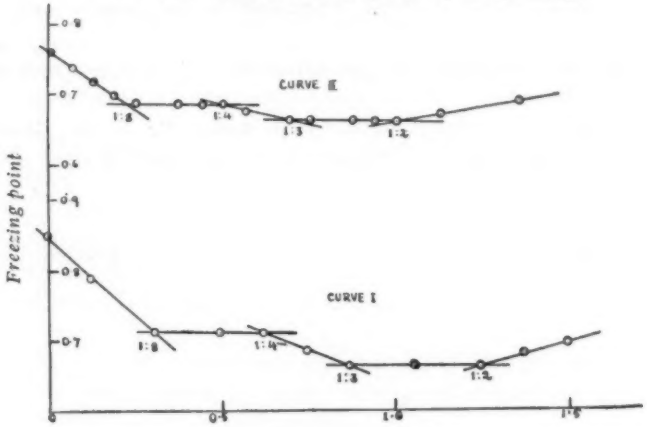
The complete elucidation of the curves and the appearance of different breaks corresponding to $[Th^{4+}] : [C_2O_4^{2-}]$ equal to 1:8, 1:4, 1:3 and 1:2 respectively require close consideration. In the present work, it has been observed that the value 1:8 of the [thorium : oxalate] concentration ratio is critical for the soluble

$[Th(C_2O_4)_4]^{4-}$ ion, above which the complex is hydrolytically stable and remains in solution, whereas if the ratio equals 1 : 8 or is lower than that, the complex suffers a partial hydrolytic decomposition with the formation of very sparingly soluble $[Th(C_2O_4)_3]^{2-}$. The reaction can be represented as

$$[Th(C_2O_4)_4]^{4-} \rightleftharpoons [Th(C_2O_4)_3]^{2-} + C_2O_4^{2-}.$$

FIG. 4

F. P. of the cryohydrate, KNO_3-ice, 0.67° (Beckmann).



Thorium nitrate (*c.c.*).

Curve I-500 c.c. of 0.11*M*-$K_2C_2O_4$ in soln. in 12% KNO_3 2.15*M*-$Th(NO_3)_4$ soln. added.

Curve II-50 c.c. of 0.053*M*-$K_2C_2O_4$ soln. in 12% KNO_3 1.325*M*-$Th(NO_3)_4$ soln. added.

So, t e break at $[Th^{4+}]:[C_2O_4^{2-}] = 1:8$ indicates no compound formation. It, on the other hand, marks the stability-range of the complex ion, $[Th(C_2O_4)_4]^{4-}$, below which $[Th(C_2O_4)_4]^{4-}$ is hydrolytically decomposed. The idea of a new compound formation at 1 : 8 may therefore be discarded and the following mechanism may be proposed.

Up to the ratio of 1 : 8, the change in the depression of the freezing point was due only to the removal of the free oxalate in the form of the soluble $[Th(C_2O_4)_4]^{4-}$ ion. The picture changes as the critical ratio is reached and hydrolytic decomposition of $K_4[Th(C_2O_4)_4]$ begins. From this point onwards, simultaneous application of two opposing processes, viz., the removal of free oxalate ion by the addition of $Th(NO_3)_4$, and the regeneration of free oxalate as a result of hydrolytic decomposition tend to balance each other, keeping the number of ions in solution constant. Thus, throughout the range (from 1 : 8 to 1 : 4), the freezing point depression is a constant one. The partial nature of the hydrolytic decomposition is also indicated from the freezing point depression value, which is still much below the eutectic temperature, indicating the presence in solution of ions other than K^+ and NO_3^-. The break at 1 : 4 then corresponds to that of the normal tetra-oxalate $K_4[Th(C_2O_4)_4]$. As in the case of

thermometric titrations, the break at 1 : 3 may be explained as being due to the complete conversion of $[Th(C_2O_4)_4]^{4-}$ into $[Th(C_2O_4)_3]^{2-}$ with the consequent attainment of the eutectic temperature. Further addition of thorium nitrate causes the transformation of $K_2[Th(C_2O_4)_3]$ to the insoluble $Th(C_2O_4)_2$ through insolube $K_2[Th_2(C_2O_4)_5]$ as the intermediate compound in the solid phase, and therefore, no indication of the break in the ratio 2 : 5 could be observed by the cryoscopy, cryoscopic lowering being a property of the solution. Hence, the eutectic temperature is maintained till the termination of the reaction ($[Th^{4+}] : [C_2O_4^{2-}] = 1 : 2$). After this, the increase in free $[Th^{4+}]$-ion concentration causes a linear depression of the eutectic temperature with the titre value.

Thus, the existence of $K_4[Th(C_2O_4)_4]$ as well as $K_2[Th(C_2O_4)_3]$ may be corroborated by both the physical methods.

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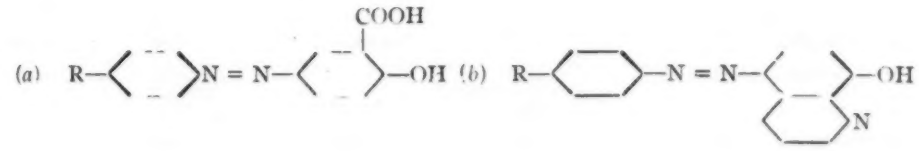
USE OF AZO DYES AS REAGENTS IN INORGANIC ANALYSIS AND AS ANTIBACTERIALS. PART I

By Raicharan Das and S. S. Guha Sircar

Several azo dyes derived from salicylic acid and 8-hydroxyquinoline have been prepared and their antibacterial action studied against *E. Coli* and *Staphylococcus aureus*. Their reactions with common group metals have been studied over p_H ranges 3.42 to 7, and more, in alcoholic solutions. Antibacterial activity is not high, but their reactions show that some of them can be used for spot tests and gravimetric and colorimetric estimations of some metals.

Azo dyes that have been used as analytical reagents include mainly Magneson (Ruigh, *J. Amer. Chem. Soc*, 1929, **51**, 1456; Engel, *ibid.*, 1930, **52**, 1812) and Cadion (Dwyer, *Chem. Abs.*, 1937, II, 3412; Fisher, *Ber.*, 1884, **17**, 641; 1887, **20**, 1581). Some azo derivatives of 8-hydroxyquinoline have been reported to have formed coloured precipitates with metals in general (Gutzeit and Monnier, *Helv. Chim. Acta*, 1933, **16**, 233, 478; Boyd *et al.*, *Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 606; cf. *J. Amer. Chem. Soc.*, 1943, **65**, 2241).

In the present paper a study has been made of the uses of some azo dyes derived from salicylic acid and 8-hydroxyquinoline as reagents in inorganic analysis. The compounds possess the following general structure :



where R is a substituent like -Cl, -NO_2, -CH_3, -COOH, -OH, and -$COCH_3$ which occupy either *o*-, *m*-, or *p*-position. Their uses in analysis are described below.

Experimental

The azo dyes were prepared by diazotising the aromatic primary bases (1 mol.), dissolved in 2½ moles of *N*-HCl, and treating the cold mixture with 1 mole of $NaNO_2$ in 10% solution, dropwise, below 5° till starch-iodide indicator paper was turned blue. The diazotised solution was then added dropwise to (*a*) salicylic acid and (*b*) 8-hydroxyquinoline, dissolved in 2½ moles of *N*-NaOH solution, at that temperature. The reaction mixture was stirred for ½ to 1 hour to ensure complete coupling. The final mixture was acidified with 2*N* acetic acid to liberate the dye completely while the stirring was continued. The precipitate was filtered at the pump, washed with water and finally recrystallised from rectified spirit, and dried in the steam oven.

Most of the dyes were crystalline, possessing brown, orange or red colour, usually soluble in alkali, ammonia, ethyleneglycol and alcohol. The determination of nitrogen

in the azo compounds was done by the method described by Simek (*Chem. Listy*, 1931, **25**, 322) in which the compounds were reduced with alkaline-alcoholic $Na_2S_2O_4$ solution and then digested and estimation carried out by Kjeldahl's method. The analytical data of the dyes are recorded in Table I.

TABLE I

	Bases diazotised	M. P.	Colour.	% Nitrogen. Found.	Calc.
(*a*)	and coupled with salicylic acid.				
1.	*o*-Nitroaniline	219°	Deep brown	14.08	14.6
2.	*m*- ,,	226°	Chocolate	14.36	14.6
3.	Sulphanilamide	150°	Yellow	11.61	11.91
4.	*p*-Aminoacetophenone	>250°	Orange	9.50	9.82
5.	*o*-Aminobenzoic acid	>250°	Orange-yellow	9.37	9.75
(*b*)	and coupled with 8-hydroxyquinoline.				
6.	*o*-Nitroaniline	219°	Chocolate	18.48	19.1
7.	*p*- ,,	260°	Dark brown	18.58	19.1
8.	*m*- ,,	249°	Orange	18.66	19.1
9.	*m*-Toluidine	112°	Greyish red	15.50	15.9
10.	*p*-Aminoacetophenone	216°	Yellow	14.10	14.3
11.	Sulphanilamide	252°	Orange-red	16.91	17.34
12.	*o*-Aminobenzoic acid	248°	Red	14.02	14.28
13.	*m*- ,,	257°	Yellow-brown	14.00	14.28
14.	*p*- ,,	>280°	Chocolate	13.96	14.28
15.	*p*-Aminosalicylic acid	>280°	Dark grey	15.53	16.02

A 0.5% solution of the reagent in rectified spirit was added to 10 drops of 2 *N* solutions of salts of the following metals arranged in their analytical order in a series of test tubes containing 2 c. c. of an acetate buffer solution ranging in p_H between 3 and 7 (Pb, Hg, Ag, Cu, Cd, Bi, As, Sn, Al, Fe, Cr, Co, Mn, Ca, Ba, Sr, Mg, Mo, W & V). The formation of any precipitate or colour change in the mixture was noted, both in the cold and on heating. When a precipitate was formed, the test was made on a large scale and the insoluble residue filtered, washed and tested for solubilities in dilute acetic acid, ammonia, rectified spirit, acetone, ethyl acetate and also with concentrated nitric acid to ascertain whether the metal was liberated from the complex thereby. The p_H ranges in which the coagulation of the precipitated was best and the precipitation quantitative were also noted. In case of coloured comp'exes, the sensitivity of the reagents for the metals was noted in solution and by spot test following "Bechhold Capillary Phenomena". The reactions of the reagents with the cations at different p_H are shown below.

TABLE II

Q = quantitative; sol = soluble; EtOAc = ethyl acetate; p = partly, sp = sparingly; decomp = decomposing. The colour mentioned represents that of the precipitate; where only coloration is formed, this is mentioned as coloration or col.

Sl. No. of reagent.	Metallic ion.	p_H.	Colour of precipitate.	Solubility and whether Q etc.
1.	Pb	3·42-7	Brown	Grannular. Q, insol in water, dil. HAc, EtOAC; sol in NH_4OH, decomp. in strong acids; ppt. formed easily at p_H 5.89.
	Ag	,,	Dark brown	Insol in water & dil. HAc
	Hg (ous)	7	,,	,, ,,
	Hg (ic)	3·42-7	,,	,, ,,
	Cu (ic)	4·02-4·99	Brown	Insol in alcohol
	As & Sn	7	,,	Insol in water, NH_4OH, alcohol dil HAc.
	Fe	7	Brown col.	Up to 10^{-6} g./100 c. c.
	Mn	NH_4Cl-NH_4OH	Dark brown (after a time)	
	Ca	,,	Yellow	Gelatinous, insol in water & EtOH
	Ba	,,	Deep red	,, ,, ,,
	Sr	,,	Dark brown	,, ,, ,,
	Mg	,,	Yellow	
2.	Pb	3·42-7	,,	Sol in NH_4OH, acetone; insol in EtOAC & water
	Ag	4·99-7	Brown	,, ,, ,,
	Hg (ous)	7	Yellowish brown	,, ,, ,,
	Cu (ic & ous)	7	Faint brown	
	As	7	Yellow	p sol in water; sol in acetone, NH_4OH, EtOAc.
	Sn	7	Yellow lake	p sol in water.
	Fe	7	Brown col.	Sensitive up to 10^{-3} g./100 c c.
	Mn	NH_4Cl-NH_4OH	Yellow (after a time)	
	Ca	,,	Reddish brown	Insol in water
	Ba & Sr	,,	Dark brown	,, ,,
3.	Pb & Ag	3·42-7	Reddish brown	Insol in water; sol in acetone, NH_4OH; p sol in EtOAc; decomp in dil. HCl & HAc.
	Hg (ous)	7	Yellow	Q, decomp. at 50°
	Hg (ic)	4·05-5·89	Pale yellow	
	Sn	7	Yellow	Turns brown slowly
	Fe	7	Brown col.	Sensitive up to 10^{-3} g./100 c. c.
4.	Pb & Ag	3·42-7	Yellowish turbidity	
	Sn	7	,, ,,	
	Fe	7	Brown coloration	Sensitive up to 10^{-4} g./100 c. c.

TABLE II (contd.)

Sl. No. of reagent.	Metallic ion.	p_H.	Colour of precipitate.	Solubility and whether Q etc.
5.	Pb	3.42-7	Yellowish brown	Q, sol in NH_4OH; insol in water & dil. HAc; p sol in EtOAc, decomp in strong HNO_3. ppt. easily formed at p_H 5.89.
	Ag	,,	Golden yellow	Q, decomp at 60°, insol in water.
	Cu (ic)	3.42-7	Scarlet-red	Insol in water, decomp in hot dil HCl.
	Fe	7	Brown col.	Sensitive up to 10^{-6} g./100 c. c.
6	Hg (ous)	7	Rose col.	
	Fe	7	Brown col.	Sensitive up to 10^{-3} g /100 c. c.
	Ca, Ba & Sr	NH_4Cl-NH_4OH	Slight pink (after 10-15 min.)	
	Mg	NaOH	Pink lake	Sensitivity (0.2).10^{-4} g./100 c.c.
7.	Hg (ous)	7	Rose col.	
	Fe	7	Brown ,,	Sensitive up to 10^{-5} g./100 c. c.
	Zn	3.42-7	Pink ,,	Sensitive up to 10^{-5} g./100 c. c.
	Ca, Ba & Sr	NH_4Cl-NH_4OH	Slight brown (after 15-20 min.)	
	Mg	NaOH	Blue lake	Sensitivity 10^{-4} g./ 100 c. c.
8.	Fe	7	Brown col.	Sensitive up to 10^{-6} g./100 c. c.
	Mg	NaOH	Rose lake	Sensitive up to 10^{-4} g./100 c. c.
9.	Pb	3.42-7	Slight brown	
	Ag	,,	Yellow turbidity	
	Fe	7	Brown col.	Sensitive up to 10^{-7} g./100 c. c.
	Mg	NaOH or NH_4OH	Reddish brown lake	Sensitivity (5).10^{-3} g./100 c. c
10.	Pb	3.42-7	Orange-yellow	Q, sol in HAc; insol in NH_4OH, EtOAc, acetone, water; decomp in hot HCl.
	Fe	7	Brown col.	Sensitive up to 10^{-6} g./100 c. c.
	Mg	NaOH	Permanganate coloured lake	Sensitive up to 10^{-4} g./100 c. c.
11.	Ag	3.42-7	Red	Sensitivity 10^{-5} g./100 c. c.
	Hg (ic)	,,	,,	Sensitivity 10^{-6} g./100 c. c
	Cu (ic)	,,	Slight yellowish brown	
	Fe	7	Brown col.	Sensitive up to 10^{-6} g./100 c. c.
	Mn	NH_4Cl-NH_4OH	Slight dark brown (after a time)	
	Mg	NaOH	Red lake	Sensitivity 10^{-3} g./100 c. c.
12.	Pb	3.42-7	Yellow	Sol in dil HCl & dil HAc, acetone, NH_4OH; insol in EtOAc, water; decomp in boiling dil acids.
	Ag	,,	Deep red	Q, sensitive up to 10^{-7} g./100 c. c. decomp in hot acids & at 60°.
	Hg (ic)	3.42-7	Permanganate, gives coloration above $N/1000$ solutions	Sensitive up to 10^{-6} g./100 c.c.
	Hg (ous)	7	Permanganate, gives coloration in dil. solns.	

TABLE II (contd.)

Sl. No. of reagent	Metallic ion.	p_H.	Colour of precipitate.	Solubility & whether Q etc.
12.				
	Cu (ic)	3.42-7	Reddish brown	Decomp. in hot dil. acids
	Fe	7	Grey col.	Sensitive up to 10^{-7} g./100 c.c.
	Cr	7	Permanganate col.	,, ,, 10^{-3} g./100 c.c.
	Co	3.42-	Permanganate ,,	,, ,, 10^{-6} g./100 c.c.
	Mn	NH_4Cl-NH_4OH	Yellow turbidity (after 10-15 minutes)	
	Zn	3.42-7	Permanganate, gives coloration in dil. solns. above $N/2000$	Q, sensitive up to 10^{-6} g./100 c. c.
	Ca & Ba	,,	Pink	Decomp. in hot dil. acids
	Mg	NaOH	Golden yellow lake	Sensitive up to 10^{-3} g./100 c.c., does not give spot test.
13.	Pb	3.42-7	Yellow	Q, easily formed at p_H 5.80; insol in water, alcohol & dil. HAc.
	Ag	,,	Reddish brown	Insol in alcohol & water
	Hg (ic)	,,	Yellow	,, ,, ,,
	Hg (ous)	7	Red	,, ,, ,,
	Cu (ic)	3.42-7	Yellow	,, ,, ,,
	Fe	7	Brown coloration	Sensitive up to 10^{-5} g./100 c. c.
	Cr	7	Reddish brown	Insol in alcohol & water
	Co & Zn	3.42-7	Reddish brown	Q, insol in water & alcohol
	Mg	NaOH	Orange-red lake	Sensitivity (3). 10^{-3} g./100 c.c.
14.	Pb	3.42-7	Reddish brown	Q, easily formed at p_H 5.89; sp sol in alcohol; insol in water
	Ag	,,	Purple	Sensitive up to 10^{-6} g /100 c.c.
	Hg (ous)	7	Purple	Insol in alcohol
	Hg & Cu (ic)	3.42-7	Reddish brown	,, ,,
	Fe	7	Brown coloration	Sensitive up to 10^{-6} g./100 c.c.
	Cr	7	Reddish brown	Insol in alcohol
	Co	3.42-7	Yellow	Q, insol in water & alcohol, pptn. favoured at p_H 5.89
	Zn	,,	Orange-red	,, ,, ,, ,,
	Mg	NaOH	Rose lake	Sensitivity 10^{-4} g./100 c.c.
15.	Pb	3.42-7	Reddish brown turbidity	
	Ag	,,	Rose-red	Q, insol in water & alcohol, sensitive up to 10^{-4} g./100 c.c.
	Hg (ous)	7	Rose-red	Gives spot test
15.	Fe	7	Brown coloration	Sensitive up to 10^{-4} g./100 c.c.
	Co	3.42-7	Red	Q, slowly forms; insol in water & alcohol
	Mn	NH_4Cl-NH_4OH	Yellow turbidity	
	Mg	NaOH	Orange-red lake	Sensitivity 10^{-3} g./100 c c.

Quantitative Estimations

Quantitative estimations were carried out with Pb, using reagents 1, 5, and 14, and with Zn, using reagent 14. $Pb(CH_3COO)_2$ solution was standardised gravimetrically, $ZnSO_4$ solution being standardised by $ZnNH_4PO_4$ method.

Standard metal solutions were taken with 200 c.c. of buffer solution and warmed on a water-bath. Then the solution of the reagent was slowly added with constant stirring until in slight excess. The precipitates were warmed over the water-bath for over half an hour, allowed to settle, filtered through sintered glass crucible and washed with dilute alcohol and warm water. The precipitates were heated to constant weight at 105°, and the compositions of the complexes were studied.

Estimation of Pb.—The following are the results assuming 2: 1 combination between the reagents 1, 14 and an inner-complex formation between reagent 5 and Pb.

TABLE III

Serial No. of the reagent	Mean weight of Pb complex.	Theoretical weight of Pb complex.
1.	0.3452 g.	0.3468 g.
5.	0.4637	0 4656
14.	0.3419	2 3443

It was found that the Pb salts of the reagents 1 and 5 contained one molecule of water of crystallisation, whereas that of reagent 14 was anhydrous. The formulae are given as: (1) $Pb(C_{26}H_{16}O_{10}N_6).H_2O$. (5) $Pb(C_{14}H_9O_5N_2).H_2O$. (14) $Pb(C_{32}H_{20}O_6N_6)$.

Estimation of Zn *with Reagent* 14.—Mean weight of the complex found was 0.1227 g. and the mean weight of the complex calculated was 0.1235 g. This agrees with the theoretical yield expected on the basis of 2:1 combination between the reagent and Zn. On analysing the complex it was found that it contained 10% of Zn, whereas theoretically it should contain 10.01% of Zn. The formula of the complex is taken to be $Zn(C_{16}H_{10}O_3N_3)_2$.

This method of estimating zinc can be treated as superior to some of the existing methods. The pyridine method (Vogel, p. 550) involves use of various wash liquids and is not always reliable. Estimation as zinc-quinaldinate is expensive (Vogel, p. 550) and the recovery process (Vogel, p. 167) is round about and tedious. This process of estimating zinc stands on a par with (i) the $ZnNH_4PO_4$ method (Vogel, pp. 550-51) and (ii) the oxine method (Welcher, "Organic Analytical Reagents", Vol. I, Van Nostrand, N. Y., 1947). The precipitate is stable up to 140° and insoluble in water, alcohol and dilute acetic acid. With boiling alcohol it is only slightly soluble. Estimation of zinc with reagents 12 and 13 is being pursued and is expected to furnish valuable results.

Colorimetric Analysis

o-Carboxybenzene-azo oxine gave violet colour with Zn and Hg in dilute solution in aqueous medium (the sensitivity being 10^{-6} and 10^{-5} g./100 c.c. respectively), interfered by Co and Ag ions. So the coloured complexes were studied in a Duboscq and

in a photoelectric colorimeter. The aim was to establish the validity or otherwise of Beer's law in the cases of the coloured complexes.

Zinc salt solutions of the same concentration (0.0001 g. of $ZnSO_4$ per 100 c.c.) were treated with solutions of the reagent (0.0001 g. per 100 c.c.) in different ratios and the colours developed compared in a Duboscq colorimeter. Between Zn : reagent = 1:3 and 1:4, full development of colour was seen, corresponding to the combination of 2 g. mols of reagent to 1 g. mol. of $ZnSO_4$. The results of transmission of light by this coloured complex at different wave-lengths in the visible region in a photoelectric colorimeter are shown in Fig. 1. While verifying Beer's law by the Duboscq colorimeter it was found that at concentrations above 0.002 g./100 c.c. all light was absorbed and beyond concentration 0.00001 g./100 c.c. all light was transmitted. Table IV records the results of verification of Beer's law in a photoelectric colorimeter.

TABLE IV

Conc. $\times 10^5$.	I_0.	I.	Log $I_0/I \times 10^2$.
Blank	100	...	...
0 625	,,	99.0	4.4
1.000	,,	98.5	6.6
1.250	,,	98 0	8.8
2.500	,,	96.0	17.7
5.000	,,	92.5	34.0
10.000	,,	85.5	68.0

While investigating the Hg (ic) complex, preliminary tests with visual colorimeter revealed that at the molar ratio of reagent : $HgCl_2 = 2.1$ there was maximum development of colour. Fig 2 shows the results recorded while studying the nature of transmission curve and verifying Beer's law in a photoelectric colorimeter. From the graph it is seen that Beer's law is obeyed between 400 and 600 mμ.

FIG. 1

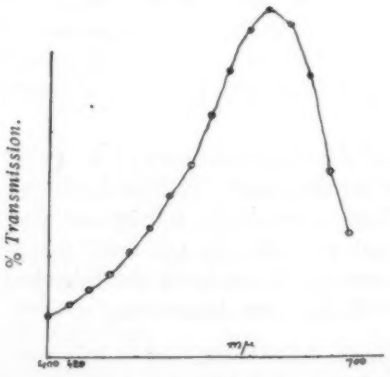
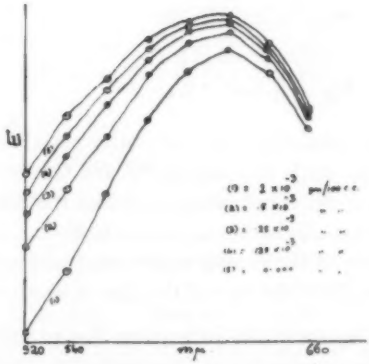


FIG. 2



From the above results it is evident that the Beer-Lambert law is applicable to the coloured complexes in question within proper conditions of wave-length and concentration and within range of experimental errors.

A Note on Antibacterial Properties of Azo Dyes

Azo dyes used as antiseptic and chemotherapeutic agents include Dimazon, Pyridium, Prontosil and Azosulphamide. Shreve *et al.* also studied antibacterial action of some azo dyes (*J. Amer. Chem. Soc.*, 1943, **65**, 2248, 2243). Here antibacterial action of the above azo dyes derived from salicylic acid and 8-hydroxyquinoline have been tested against *E Coli* and *Staphylococcus aureus* in nutrient broth medium using Rideal-Walker serial dilution method. The time of contact was 5 minutes, the temperature of incubation was 37.5° and observations were noted after 24 hours. The following results were observed.

TABLE V

Bases diazotised	M. E. D	
	E. Coli	Staph. aur.
(*a*) and coupled with salicylic acid.		
1. *o*-Nitroaniline	1 :1000	1 :1000
2. *p*- ,,	1 :8000	1 :8000
3. Sulphanilamide	1 :1000	1 :1000
4. *p*-Aminoacetophenone	<1 :1000	<1 :1000
5. *o*-Aminobenzoic acid	1 :1000	1 :1000
(*b*) and coupled with 8-hydroxyquinoline.		
6. *o*-Nitroaniline	1 :1000	1 :1000
7. *p*- ,,	1 :1000	1 :1000
8. *m*- ,,	1 :1000	1 :1000
9. *m*-Toluidine	1 :20,000	1 :10,000
10 *p*-Aminoacetophenone	<1 :1000	1 :1000
11. Sulphanilamide	1 :2000	1 :2000
12. *o*-Aminobenzoic acid	1 :8000	1 :8000
13 *m*-Aminobenzoic acid	1 :2000	1 :4000
14. *p*-Aminobenzoic acid	<1 :1000	<1 :1000
15. *p*-Aminosalicylic acid	1 :2000	<1 :1000
(*c*) Zn compound of R 14.	1 :1000	1 :2000
Hg compound of R 12	1 :80,000	1 :60,000

It would be seen that antibecterial activities of the compounds were of a low order against both Gram-positive and Gram-negative bacteria tested. Neither do the present data permit conclusions regarding the dependence of bacterio-static activity on chemical structure. Guha Sircar and co-workers (this *Journal*, 1950, **27**, 357, 535) found that introduction of Hg greatly augmented antibacterial activity. A study of the behaviour of the metallic chelates of the dyes towards the bacteria may prove interesting.

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ANALYTICAL ASPECTS OF SOME ORGANIC COMPOUNDS. PART I. SOME PHENOLIC ACIDS IN THE ESTIMATION OF THORIUM AND ZIRCONIUM

By Sachindra Kumar Datta

Analytical properties of some substituted phenolic acids, *e. g.*, 5-bromo-, 5 nitro-, 5-amino-salicylic acids, β-resorcylic and bromoresorcylic acids have been studied. Gravimetric determinations of thorium and zirconium have been made with some of these acids. β-Resorcylic and 5-nitrosalicylic acids may be used for the separation of thorium and zirconium by suitable control of the acid concentration of the mixture. Separations of thorium from cerite earths and monazite and of thorium and zirconium from other metals have also been indicated.

Though considerable work has been done on the possibility of using the organic compounds possessing special structure as analytical reagents, a thorough study of most of the common and simple compounds have not been undertaken to any great extent. The object of the present series is to investigate in a systematic way the utility of simpler organic compounds in the analytical field, and specially to ascertain the effect of substituent group or atoms in the molecules upon their analytical behaviour.

The present paper deals with some phenolic acids. Some of these acids have already been used by various workers as analytical reagents, *e. g.*, salicylic acid for the determination of Fe, Ti, Th (Kolbe and Ahrle, *Z. angew. Chem.*, 1905, **18**, 92) and Zr (Sastry and Rao, this *Journal*, 1951, **28**, 530), 3 : 5-dinitrosalicylic acid for Fe, ammonium salicylate for the extraction of Ti (Dietrich and Freund, *Z. anal. Chem.*, 1908, **56**, 344), acetylsalicylic acid (Rao and Rao, this *Journal*, 1950, **27**, 570) and *p*-aminosalicylic acid (Datta and Banerjee, *Anal. Chim. Acta*, 1955, **13**, 23) for the estimation of Th, and sulphosalicylic acid for the extraction of Ti (Moser, *Monatsh.*, 1923, **44**, 91 ; *Ber.*, 1925, **58**, 380). Trihydroxy acids, like gallic acid, produce incomplete precipitation of Th (Neish, *Chem. News*, 1904, **90**, 196), whereas trimethylgallic acid (Venkatramaniah and Rao, this *Journal*, 1950, **27**, 81) gave fruitful results. It appears that a systematic study on the effect of substitution in these phenolic acids on the determination of various inorganic ions, has not been undertaken. On testing the precipitating action of these acids on various metal ions (Table I), it was found that some were suitable for the estimation of thorium and zirconium. Hence, comparative studies on the estimation of thorium and zirconium only, by these reagents, have been made in this communication.

TABLE I

Action of some phenolic acids on the inorganic ions.

	Phenolic acids.	Cu.	Hg^{I}.	Hg^{II}.	Sn^{II}.	Al.	Fe^{III}.	Pd.
1.	Salicylic	—	* White ppt.	—	—	—	Violet col.	—
2.	5-Nitrosalicylic	Yellow-green col.	* Grey ppt	—	—	* White ppt.	Blood-red col.	—
3.	5-Bromosalicylic	—	* White ppt.	—	—	—	Violet col.	—
4.	5-Aminosalicylic	—	* Do	* White ppt.	—	Turbidity	Violet-red col.	Yellow ppt.
5.	β-Resorcylic	—	* Do	—	—	Do	Violet col.	—
6.	5-Bromoresorcylic	—	* Do	—	—	Do	Violet ,,	—
7.	Gallic	Reduced	* Yellowish white ppt.	—	—	—	Blue ,,	* Grey ppt.

TABLE I (contd.)

	Phenolic acids.	Thorium.	Zirconinm.	Titanium.	Uranium.
1.	Salicylic	White ppt.	White ppt.	Yellow col.	Orange col.
2.	5-Nitro- ,,	Bluish yellow ppt.	Grey ppt.	Do	Yellow col.
3.	5-Bromo- ,,	White ppt.	White ppt	* Pale yellow ppt.	Orange col.
4.	5-Amino ,, (P.A.S.)	Do	Do	* Yellow ppt.	Do
5.	β-Resorcylic	Pinkish white ppt.	Do	Do	Do
6.	5-Bromoresorcylic	White ppt.	Do	Do	Do
7.	Gallic	Turbidity	Turbidity	Brown col.	Yellow col.

(–) indicates no precipitation. * indicates incomplete precipitation.

EXPERIMENTAL

Salicylic acid, 5-nitro-, 5-bromo- and 5-amino-salicylic acids and gallic acid used were of analytical reagent quality.

β-Resorcylic acid was prepared and purified in the laboratory (m. p. 213°) according to Brunner (*Annalen*, 1907, **351**, 319). 5-Bromoresorcylic acid (m.p. 207°) was prepared in the laboratory from β-resorcylic acid, glacial acetic acid and bromine after Rice (*J. Amer. Chem. Soc.*, 1926, **48**, 3127).

Stock solutions of reagent grade thorium, cerium and lanthanum nitrates were prepared and their earth contents determined as usual (Datta and Banerjee, this *Journal*, 1954, **31**, 149). Zirconium solution was prepared in the similar manner and standardised by benzilic acid method (Venkatramaniah and Rao, *ibid.*, 1951, **28**, 257; Klingenberg and Mendell, *Anal. Chem.*, 1954, **26**, 753). The other salt solutions were estimated by standard methods.

Estimation of Thorium and Zirconium

Aliquot quantities of thorium and zirconium solutions were neutralised to Congo red after adding about 0.2 g. of solid ammonium acetate. To the hot (90°) solutions were added hot 2% solutions of salicylic acids until the precipitation was complete. Only in the case of β-resorcylic acid (which is very sparingly soluble in water) a large volume of 0.1% solution was added. The precipitates were digested for 10 minutes, filtered through Whatman No. 42, and washed with boiling water, dried and finally ignited to the oxide.

With salicylic and β-resorcylic acids, only a milkiness appeared first in solutions of thorium, not containing any ammonium acetate, which gradually coagulated to a coherent mass on long boiling or on addition of a small amount of ammonium acetate. 5-Nitrosalicylic acid did not furnish any precipitate of thorium in absence of ammonium acetate. The precipitation of zirconium, however, was more rapid compared to that of thorium by these reagents; addition of a little ammonium acetate (0.2 g.) improved the quality of the precipitates. The sensitivities of these reagents were compared by determining thorium and zirconium from their solutions of very high dilutions.

A few representative results are recorded in Table II. Though salicylic acid was used for the estimation of Th and Zr, and P. A. S. for the determination of Th by previous workers, their findings were repeated for the sake of comparison with those obtained by using other phenolic acids.

TABLE II

Determination of thorium and zirconium by salicylic acids.

Reagents.	ThO_2 (g.)		ZrO_2 (g.)		Reagents.	ThO_2 (g.)		ZrO_2 (g.)	
	Taken.	Found.	Taken.	Found.		Taken.	Found.	Taken.	Found.
1. Salicylic	0.0220	0.0216	0.0126	0.0127	4. 5 Aminosali-	0.0082	0.0084	0.0021	0.0023
	0.0165	0.0157	0.0021	0.0022	cylic	0.0055	0.0053	0.0012	0.0013
2. 5 Nitrosali-	0.0082	0.0082	0.0021	0.0023	5. β-Resorcylic	0.0165	0.0151	0.0021	0.0018
cylic	0.0055	0.0052	0.0012	0.0011		0.0055	0.0045	0.0012	0.0006
3. 5 Brom sali-	0.0165	0.0160	0.0021	0.0021	6. 5-Bromoresor-	0.0082	0.0079	0.0021	0.0019
cylic	0.0082	0.0073	0.0012	0.0009	cylic	0.0055	0.0048	0.0012	0.0008

From the above table it is clear that the sensitivity of the phenolic acids increases by the introduction of various groups into the neuclus ; nitro- and amino-salicylic acids are more efficient precipitating agents for thorium and zirconium than the corresponding bromo-acids. But the sensitivity decreases gradually with the increase in the number of OH groups in the molecule; β-resorcylic acid and gallic acid (which does not completely precipitate Th or Zr, even in conc. solution at high p_H) are good examples of this fact; on substitution, however, these acids may prove useful. The nature of the precipitates with the substituted salicylic acids was also found better than those with unsubstituted acid. Zirconium salts were much more granular and easily filtrable than the corresponding thorium salts.

Effect of Hydrogen-ion Concentration on Precipitation

In order to compare the efficiency of these acids again in different acid-concentrations and to explore the possibilities of separating thorium and zirconium from a mixture by some of those phenolic acids, the determinations of thorium and zirconium were carried out by these reagents in solutions having different p_H values, adjusted by the addition of ammonium acetate buffer. The results are shown in Table III.

TABLE III

Reagents.	1.8	2.	2.5.	3.2.	3.6.	4.	4.4.
	p_H of the solution.						
	ThO_2 found (in g.) by the reagents. (ThO_2 taken = 0.0440 g.)						
1. Salicylic acid	—	0.0070	0.0088	0.0715	0.0182	0.0398	0.0439
2. 5-Nitro- ,,	—	0.0090	0.0102	0.0195	0.0201	0.0432	0.0441
3. 5-Bromo- ,,	—	0.0082	0.0098	0.0189	0.0132	0.0420	0.0440
4. 5-Amino- ,,	—	0.0099	0.0106	0.0206	0.0210	0.0439	0.0441
5. β Resorcylic acid	—	—	0.0086	0.0171	0.0181	0.0396	0.0439
6. 5-Bromoresorcylic	—	—	0.0099	0.0188	0.0192	0.0420	0.0440
	ZrO_2 found (in g.) by the reagents (ZrO_2 taken = 0.0312 g.).						
1. Salicylic acid	0.0281	0.0310	0.0311	0.0313	0.0311	0.0310	0.0291
2. 5-Nitro- ,,	0.0300	0.0311	0.0312	0.0312	0.0311	0.0310	0.0291
4. 5-Bromo- ,,	0.0139	0.0282	0.0318	0.0313	0.0312	0.0309	0.0292
4. 5-Amino- ,,	0.0128	0.0138	0.0286	0.0312	0.0311	0.0310	0.0307
5. β Resorcylic ,,	0.0309	0.0310	0.0313	0.0313	0.0311	0.0310	0.0302
6. 5-Bromoresorcylic	0.0308	0.0311	0.0312	0.0314	0.0312	0.0308	0.0304

From the above table it is observed that, in the estimation of thorium by the substituted salicylic acids, with the increase in the value of the p_H of the solution, the quantity of the precipitate obtained also increases. The effect of substitution was also noticed in such precipitations; bromo-, nitro- and amino-salicylic acids precipitated a greater amount of thorium at any p_H than the unsubstituted or hydroxysalicylic acids at the corresponding p_H values; the quantitative precipitation, however, with all the acids occurred at p_H 4 and above. But in the case of the estimation of Zr, the precipitation does not follow any definite rule; salicylic, nitrosalicylic, β-resorcylic and 5-bromoresorcylic acids produce quantitative precipitation at p_H range between 2 and 4, whereas such a precipitation of zirconium commences from p_H 3.2 with bromo and amino derivatives. The reason for this anomalous behaviour in the case of zirconium determinations was not understood.

Separation of Th and Zr and their Co-determinations by 5-Nitrosalicylic and Resorcylic Acids

Thorium was successfully separated by Sastry and Rao (*loc. cit.*) with salicylic acid. Of all the acids studied here, 5-nitrosalicylic and β-resorcylic acids were found suitable for the quantitative separation of thorium and zirconium. Thorium is completely precipitated by these acids at p_H 4 and above, whereas complete precipitation of Zr by them occurs between p_H 2 and 4. For this separation, the p_H of the mixture was kept at 2.0 and Zr was precipitated as usual. Double precipitation is always necessary, as a quantity of thorium is retained by the Zr precipitate. The p_H of the combined filtrates was raised by the addition of ammonium acetate buffer, when thorium was completely precipitated by further addition of the reagent solution. The results are shown in Table IV.

TABLE IV

Oxides taken.	Oxides found by 5-Nitro-salicylic.	Oxides found by β-Resor-cylic.	Oxides taken.	Oxides found by 5-Nitro-salicylic.	Oxides found by β-Resor-cylic.	Oxides taken.	Oxides found by 5-Nitro salicylic.	Oxides found by β-Resor-cylic.
Th 0.0220 g.	0.0218 g.	0.0217 g.	Th 0.0220 g.	0.0221 g.	0.0220 g.	Th 0.0330 g.	0.0328 g.	0.0316g.
Zr 0.0126	0.0127	0.0128	Zr 0.0252	0.0254	0.0255	Zr 0.0504	0.0508	0.0509

Separation of Thorium from Rare-earths

The phenolic acids can separate Th from the rare earths. Such separation by P.A.S was carried out by Datta and Banerjee (*loc. cit.*). Separation by salicylic, 5-nitrosalicylic, 5-bromosalicylic, β-resorcylic and 5-bromoresorcylic acids is shown in Table V. The p_H of the mixture was adjusted to 4, before adding these reagents for precipitation. Only a few representative data, showing such separation by double precipitation from the solutions having maximum thoria-rare earth ratio, are recorded in the table below.

TABLE V

ThO_2 taken = 0.0220 g.

	Reagents	CeO_2 added.	La_2O_3 added.	$ThO_2 : R_2O_3$	ThO_2 obtained by double pptn
1.	Salicylic	0 0792 g.	0 0616 g.	1 : 6.4	0.0222 g.
		0.1056	0.1232	1 : 10.4	0.0228
2.	5-Bromo- ,,	0.1056	0 1364	1 : 11	0.0223
		0 1320	0.1540	1 : 13	0.0224
3.	5-Nitro- ,,	0.2370	0.2772	1 : 23.4	0 0222
		0.2640	0.3080	1 : 26	0 0224
4.	β-Resorcylic	0 0792	0.0616	1 : 6.4	0.0220
		0.0792	0 0924	1 : 8	0 0225
5.	5-Bromoresorcylic	0.1056	0 1232	1 : 10.4	0.0221
		0.1320	0.1540	1 : 13	0 0228

From the above table it is evident that substitution in the salicylic and β-resorcylic acids enables them to effect separation of thorium from cerite earths having greater thoria-earth ratio. 5-Nitrosalicylic acid is the most effective of all ; it can precipitate Th from solutions having thoria-earth concentration up to 1 : 26, by double precipitation method, without any contamination. This ratio for 5-amino- (Datta and Banerjee, *loc. cit.*), 5-bromo-salicylic acids, bromoresorcylic acid, β-resorcylic and salicylic acids are : 1 : 23, 1 : 13, 1 : 13, 1 : 8 and 1 : 6.4 respectively.

Extraction of Thorium from Monazite Sand

The monazite extract was neutralised to Congo red and thorium was precipitated by these reagents, as before, after adding a small quantity of ammonium acetate. It is advisable to apply double precipitation in all cases, except with 5-nitrosalicylic acid, to avoid contamination. The results are recorded in Table VI.

TABLE VI

	Acids employed.	Wt. of the sample	ThO_2 obtd.	%Recovery of ThO_2.
1.	*m*-Nitrobenzoic	1.255 g.	0 0918 g	7.32
		1 232	0 0902	7.32
2,	5-Bromosalicylic	1 255	0 0916	7 31
		1.232	0 0899	7.30
3.	5-Nitrosalicylic	1.255	0 0918	7 32
		1 232	0.9030	7.32
4.	β-Resorcylic	1.255	0.0916	7.31
		1.232	0.0899	7.30
5.	5-Bromoresorcylic	1.255	0.0918	7.32
		1.232	0 0901	7.31

Separation Thorium and Zirconium from of other Elements

Most of the elements do not interfere in the separation of Th and Zr, when present along with them, by 5-nitro-, 3-bromo-salicylic and β-resorcylic and bromoresorcylic acids. The metals like Al, Cr and Co require double precipitation, as the Th and Zr

precipitates always adsorb a trace of these metals. Fe and Ti are either co-precipitated along with or held up in considerable amounts by Th and Zr, which cannot be removed by double precipitation. Separate procedures have been adopted for their separation. The results are recorded in Table VII.

TABLE VII

ThO_2 and ZrO_2 taken.	Metal oxides added.	Thorium oxide and Zirconium oxide found by 5-NO_2-sal.	5-Br-sal.	β-Res.	Br-res.
Th 22.0 mg.	Al 15.1 mg.	22.1 mg.	22.0 mg.	21.9 mg.	22.0 mg.
Zr 31.2	,, ,,	31.3	31.1	31.4	31.5
Th 22.0	Cr 21.3	22.2	21.1	22.3	22.2
Zr 31.2	,, ,,	31.4	31.5	31.4	31.4
Th 22.0	Co 20.6	22.2	22.3	22.5	22.3
Zr 31.2	,, ,,	31.5	31.4	31.3	31.4
Th 22.0	Ba 22.4	22.0	22.1	22.2	22.3
Zr 31.2	,, ,,	31.1	31.0	31.2	31.2
Th 22.0	Ca 19.1	22.0	22.2	22.1	22.2
Zr 31.2	,, ,,	31.3	31.0	31.2	31.4
Th 22.0	U 30.3	22.5	22.5	22.4	22.5
Zr 31.2	,, ,,	31.4	31.7	31.5	31.6

Separation of Thorium and Zirconium from Iron and Titanium by 5-Nitro-, 5-Amino-salicylic, and β-Resorcylic Acids

Iron and titanium form coloured complexes with the phenolic acids (vide Table I) which contaminate the thorium and zirconium precipitates, if present in a mixture. When iron and titanium are present in excess, appreciable amounts of precipitates of these metals are formed with these reagents. Titanium and iron can be kept in solution by adding H_2O_2 and NH_4SCN respectively.

To the solution containing either a mixture of Th and Fe or Zr and Fe, 5 g. of NH_4SCN was added until the solution became clear red. It was diluted to 100 c.c. and Th or Zr was precipitated as before. The precipitate was filtered and washed several times with boiling water. Double precipitation was necessary to remove the last traces of iron. For the removal of Ti, 20 c.c. of 3% H_2O_2 solution was added to the mixture of Ti and Th or Ti and Zr; precipitation of Th or Zr was carried out as before. Here also double precipitation was essential. The results are shown in Table VIII.

TABLE VIII

Iron or Ti oxides added.	P.A.S.	ThO_2 or ZrO_2 obtained by 5-NO_2-sal.	β-Resor.	Iron or Ti oxides added.	P.A.S.	ThO_2 or ZrO_2 obtained by 5-NO_2-sal.	β-Resor.
	ThO_2 taken = 22.0 mg.				ZrO_2 taen = 12.6 mg.		
Fe 14.6 mg.	22.6 mg.	22.4 mg.	22.6 mg	Fe 10.9 mg.	12.7 mg.	12.8 mg.	12.9 mg
Fe 21.9	22.7	22.6	22.6	Fe 15.6	12.9	12.8	12.9
Ti 18.3	22.4	22.3	22.4	Ti 9.2	12.8	12.7	12.8
Ti 22.9	22.6	22.5	22.5	Ti 18.4	12.9	12.7	12.9

Composition of the Thorium and Zirconium Salts

The thorium and zirconium salts of the various acids were prepared by following the same procedure, described before. The precipitates were washed with boiling water several times and then with hot absolute alcohol to remove the adhering phenolic acids. The salts were dried at 105°-110° to a constant weight. Aliquot quantities of the dried salts were ignited to the oxides. As the composition of these salts are not definite, determination of these metals by direct weighing is not possible. Moreover, the compositions of the Th or the Zr salts of all these acids are also not similar. An idea of their compositions may be had from the following table.

TABLE IX

Phenolic acids.	Probable composition of	
	Thorium salt.	Zirconium salt.
5-Aminosalicylic (P.A.S)	$(C_7H_6O_3N)$-Th$(OH)_3$,$3H_2O$	$(C_7H_6O_3N)_2$-Zr=O, $2H_2O$
5-Nitrosalicylic	$(C_7H_4O_5N)$-Th-$(OH)_3$	$(C_7H_6O_3N)_2$-Zr-$(OH)_2$
5-Bromosalicylic	$(C_7H_4O_5Br)_2$-Th$(OH)_2$,$3H_2O$	$(C_7H_4O_5Br)_3$-Zr-(OH) H_2O
β-Resorcylic	$(C_7H_5O_4)_2$-Th$(OH)_2$	$(C_7H_5O_4)_4$-Zr-(OH),$2H_4O$
Bromoresorcylic	$(C_7H_4O_4Br)_2$-Th-$(OH)_2$	$(C_7H_4O_4Br)_3$-Zr-(OH)

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CHLORAMINE-B AS A BROMOMETRIC REAGENT. PART II. INDIRECT DETERMINATIONS

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Chloramine-B has been used as a bromometric reagent to estimate indirectly potassium permanganate, potassium dichromate, potassium chromate, potassium chlorate, potassium bromate, manganese dioxide, lead dioxide and potassium chlorate in the presence of perchlorate, and hypochlorite and chlorate in presence of one another.

In the previous communication (Paul and Singh, this *Journal*, 1955, **32**, 599) chloramine-B was used as a bromometric reagent for the quantitative estimation of various reducing substances. In the present paper, chloramine-B has been further used for the estimation of potassium permanganate, potassium dichromate, potassium chromate, potassium chlorate, potassium bromate, manganese dioxide, lead dioxide and sodium hypochlorite indirectly. Mixtures of hypochlorite and chlorate have also been analysed with the help of this reagent due to the difference in their reactivity.

In these titrations a weighed sample of the substance was treated with a known volume of standard arsenious oxide solution together with 0.5-10 g. of KBr and the solution was then acidified with HCl. The bromine, first liberated by the action of the oxidising agent (say MnO_2) in the presence of HCl according to equation (1),

$$MnO_2 + 4HCl + 2KBr \longrightarrow MnCl_2 + 2H_2O + 2KCl + Br_2, \quad \ldots (1)$$

is immediateiy reduced by the arsenious oxide solution according to equation (2),

$$As_2O_3 + 2Br_2 + 2H_2O \longrightarrow As_2O_5 + 4HBr \quad \ldots (2)$$

and the excess of the arsenious oxide left unchanged in the mixture is estimated by chloramine-B solution, as reported in the previous communication.

In the case of manganese dioxide, lead dioxide and lead chromate, the solution was heated on a water-bath at 50°-70° till the sample dissolved completely, while chlorate was heated under reflux for 10-15 minutes, cooled for 10 minutes with reflux condenser on in order to avoid the loss of volatile arsenic chloride, as recommended by Manchot (*Ber.*, 1924, **57B**, 29) and Bacho (*Ann. Chem. Appl.*, 1919, **12**, 153) respectively. In the mixture of chlorate and hypochlorite, the latter was determined by titrating in the cold with a hydrochloric acidity of 5% and the former at an acidity of 10-15% and at boiling.

EXPERIMENTAL

General Method.—A known weight of the substance or its solution in water was taken in a stoppered conical flask. To it were added 30-40 c.c. of standard arsenious

oxide solution, 10 c.c. of 10% KBr and 15-20 c.c. of HCl. The flask was corked and allowed to stand for 10 to 15 minutes. The mixture was diluted with 50 c.c. of water and the excess of arsenious oxide solution, left unchanged in the mixture, was titrated against standard chloramine-B solution using 2-3 drops of 0.2% indigo carmine solution. Chloramine-B solution was added very slowly with constant shaking near the end-point till the blue colour was discharged.

Several titrations were performed, and from the volume of standard chloramine-B used, corresponding to the end-point in each titration, the amount of the substance was calculated. The results are recorded in the tables below.

TABLE I

	$KMnO_4$			$K_2Cr_2O_7$			K_2CrO_4	
0.106 *N*-C.B. used.	Taken.	Found.	0.106 *N*-C.B. used.	Taken.	Found.	0.106 *N*-C.B. used.	Taken.	Found.
9.45 c.c.	0.0316 g.	0.0317 g.	10.10 c.c.	0.0539 g.	0.0540 g.	9.40 c.c.	0.0647 g.	0.0644 g.
12.30	0.0411	0.0412	13.20	0.0686	0.0685	12.20	0.0840	0.0836
16.00	0.0537	0.0536	16.30	0.0843	0.0845	17.00	0.1163	0.1165
21.70	0.0727	0.0727	22.60	0.1176	0.1174	21.70	0.1486	0.1487

1 c.c. of 0.106 *N*-C.B. ≡ 0.00335 g. of $KMnO_4$ ≡ 0.005191 g. of $K_2Cr_2O_7$ ≡ 0.006351 g. of K_2CrO_4.

	$KClO_3$			PbO_2	
0.106 *N*-C.B. used.	Taken	Found	0.106 *N*-C.B. used.	Taken	Found
18.90 c.c.	0.0409 g.	0.0409 g.	7.90 c.c.	0.1003 g.	0.1002 g.
22.00	0.0473	0.0476	14.90	0.1916	0.1902
25.70	0.0554	0.0556	17.00	0.2160	0.2156
9.50	0.0205	0.0206	25.20	0.3205	0.3195

1 c.c. of 0.106 *N*-C.B. ≡ 0.002164 g. of $KClO_3$ ≡ 0.01268 g. of PbO_2.

TABLE II

Potassium chlorate in the presence of potassium perchlorate.

0.106 *N*-C.B. added	$KClO_3$ taken.	$KClO_4$ added.	$KClO_3$ found.
9.50 c.c.	0.0205 g.	0.080 g.	0.0206 g.
12.30	0.0266	0.104	0.0266
14.20	0.0307	0.128	0.0307
18.90	0.0409	0.160	0.0409

1 c.c. of 0.106 *N*-C.B. ≡ 0.002164 g. of $KClO_3$.

TABLE III

Hypochlorite and chlorate in the presence of one another.

				Iodine method.			
Vol. taken	0.106 *N*-chloramine-B used for NaClO.	(NaClO-$KClO_3$)	$KClO_3$	NaClO found.	NaClO found.	$KClO_3$ taken.	$KClO_3$ found.
10.00 c.c.	5.00 c.c.	9.80 c.c.	4.80 c.c.	0.01974 g	0.01974 g.	0.01025 g.	0.01038 g.
13.00	6.50	12.80	6.30	0.02566	0.02570	0.01353	0.01363
17.00	8.60	16.80	8.20	0.03395	0.03360	0.01754	0.01774
21.00	10.50	20.50	10.00	0.04145	0.04135	0.0215	0.02164

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Corrigendum

In the earlier paper (1955, Sept. issue, p. 601) in the excess method, the procedure followed was not the same as used in a previous publication (*ibid.*, 1954, **31**, 327). The procedure followed is as shown below.

A measured sample of the solution was treated with a known excess of standard Chloramine-B solution and 10 c.c. of 10% potassium bromide in a flask similar to one used by Mayr and Peyfuss (*Z. anorg allgem. Chem.*, 1915, **92**, 127). HCl (10-15 c.c.) was added for every 100 c.c. of the solution without letting in any air. The mixture was allowed to stand for 10-15 minutes and the excess of bromine was dissolved in a known volume of standard As_2O_3 solution and the excess of the tervalent arsenic titrated with standard Chloramine-B solution using 2-3 drops of 0.2% Indigo carmine solution as the indicator.

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POLYNUCLEAR AROMATIC HYDROCARBONS. PART I. A NEW ROUTE TO ANTHRACENE AND 1 : 2-BENZANTHRACENE DERIVATIVES

By O. P. Vig, S. V. Kessar, V. P. Kubba and S. M. Mukherji

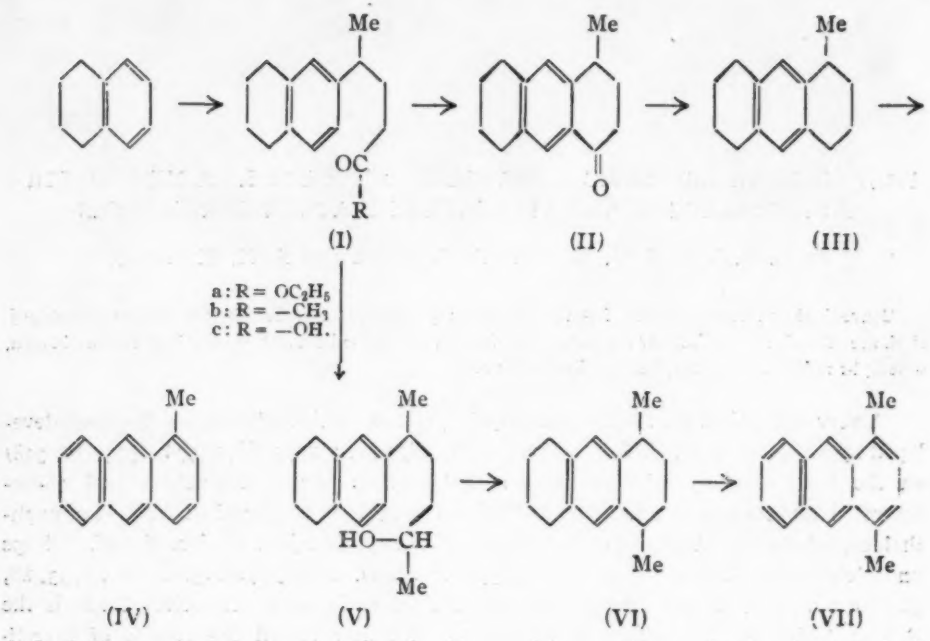
Convenient and new syntheses of 1-methyl- and 1 : 4-dimethyl-anthracene by the method of Mukherji *et al.* are described herein. By an extension of the same method a novel synthesis of the carcinogen, 4-methyl-1 :2-benzanthracene, has also been achieved.

A very convenient synthetic route to polycyclic aromatic hydrocarbons has been developed by Mukherji *et al.* (*J. Org. Chem.*, 1952, **17**, 1202 ; 1953, **18**, 1499; 1954, **19**, 328) on the basis of the cationoid reaction between an aromatic nucleus and γδ-unsaturated ketones and esters. This method has so far been employed in the field of naphthalene, phenanthrene and 3 : 4-benzphenanthrene (Mukherji *et al.*, *loc. cit.*; cf. Phillips and McWhorter, *J. Amer. Chem. Soc.*, 1954, **76**, 4948). Mosby (*J. Org. Chem.*, 1953, **18**, 964) by a variant of our method has synthesised anthracene derivatives through the Friedel-Crafts reaction with γ-valerolactone. We now record the results of investigations undertaken with a view to extending the scope of our method to the synthesis of homologues of anthracene and 1 : 2-benzanthracene.

Tetraline was condensed with ethyl allylacetate and allylacetone in presence of anhydrous aluminium chloride under the conditions laid down by Mukherji and Bhattacharyya (*J. Org. Chem.*, 1952, **17**, 1202) when the electrophilic attack took place mostly at 6-position of the tetraline molecule (cf. Mosby, *loc. cit.*), and ethyl 4-(6′-tetralyl)-valerate (I a) and 5-(6′-tetralyl)-2-hexanone (I b) were obtained in 68% and 73% yield respectively. Truffault (*Compt. rend.*, 1936, **202**, 1286) reported that tetraline with anhydrous aluminium chloride afforded benzene and a mixture of octahydroanthracene and octahydrophenanthrene through the intermediate formation of β-(4-phenylbutyl)-tetraline by the initial fission of the tetraline molecule. No such fission of the tetraline molecule was, however, observed under our conditions.

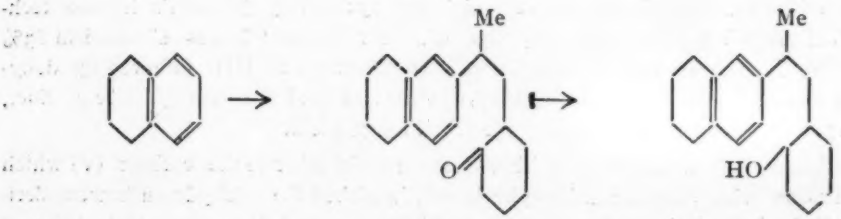
The ester (I a) on alkaline hydrolysis was quantitatively converted into the corresponding acid (I c), the acid chloride of which was cyclised by Johnson's inverse technique (*J. Amer. Chem. Soc.*, 1949, **71**, 1092) when the ketone (II) was obtained in 83% yield. The Clemmensen reduction (Martin's modification) of (II), followed by dehydrogenation over palladium-charcoal (30%) (Linstead and Thomas, *J. Chem. Soc.*, 1940, 1130), furnished 1-methylanthracene (IV) in 50% yield.

The ketone (I b) was reduced with sodium in moist ether to the carbinol (V) which on cyclisation with concentrated sulphuric acid furnished the octahydroanthracene derivative (VI) in 60% yield. Dehydrogenation of (VI) over palladium-charcoal (30%) proceeded smoothly to yield 1 : 4-dimethylanthracene (VII).

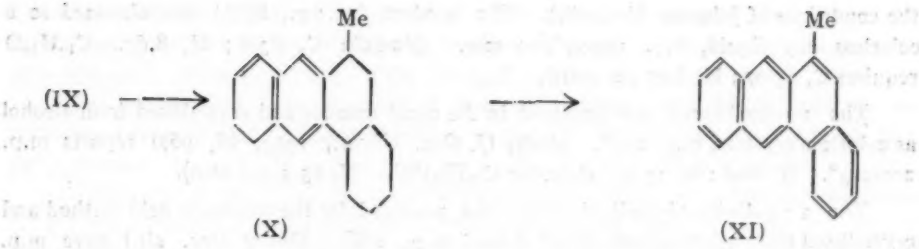


(I) (II) (III) (IV) (V) (VI) (VII)

Having succeeded in building up the anthracene system in satisfactory overall yield by the above method, our attention was then focussed on 4-methyl-1 : 2-benzanthracene which aroused considerable interest because of its pronounced carcinogenic activity (Shear and Leiter, *J. Nat. Cancer Inst.*, 1941, **2**, 214). In fact, the majority of the carcinogenic hydrocarbons of the polycyclic aromatic type belong to the 1 : 2-benzanthracene group, although the parent hydrocarbon, 1 : 2-benzanthracene, itself is devoid of any activity. However, its structure reveals that it may be regarded as a derivative of anthracene as well as of phenanthrene. Hence, it was thought that 4-methyl-1 : 2-benzanthracene could be easily synthesised by a combination of our procedure for simple anthracene homologues (*vide supra*) and 9-methylphenanthrene (Mukherji and Bhattacharyya, *loc. cit.*).



(VIII) (IX)



2-Allyl*cyclo*hexanone (Mukherji and Bhattacharyya, *loc. cit.*) was therefore condensed with tetraline in the presence of anhydrous aluminium chloride under our conditions when 2-[β-methyl-β-(6′-tetralyl)-ethyl]*cyclo*hexanone (VIII) was obtained in 55% yield. This product was reduced in almost quantitative yield to the corresponding carbinol (IX) by the Ponndorf method. Cyclisation of the carbinol (IX) with sulphuric acid (*d* 1.84) furnished the dodecahydro-1 : 2-benzanthracene derivative (X) in 80% yield, which was smoothly dehydrogenated over palladium-charcoal (30%) at 300°-320° for four hours, when 4-methyl-1 : 2-benzanthracene (XI) was obtained in 65% yield. The aromatised hydrocarbon was identified through its picrate and trinitrobenzene derivative.

EXPERIMENTAL *

Ethyl 4-(6′*Tetralyl*)-*valerate* (I a).—Freshly distilled tetraline (125 c. c.), taken in a 500 c. c. three-necked flask fitted with a guard tube, a mercury sealed mechanical stirrer and a dropping funnel, was cooled in an ice-bath. To the cooled tetraline at 0°-5°, with continuous stirring, anhydrous $AlCl_3$ (40 g., 2 *M*) and ethyl allylacetate (20 g., 1 *M*) were added in lots (1-2 g.) alternately in 2 hours. The stirring was continued for 3 hours afterwards. When the colour of the reaction mixture changed to cherry-red, it was poured onto ice-cold HCl and the product extracted twice with ether. The combined ethereal extract was washed free of acid and dried over anhydrous sodium sulphate. The ether was removed and the residual liquid distilled under reduced pressure, when 25 g. (68%) of the ester was obtained at 174-75°/8 mm. (Found: C, 78.08 ; H, 8.80. $C_{17}H_{24}O_2$ requires C, 78.46 ; H, 9.24 per cent).

4-(6′-*Tetralyl*)-*valeric Acid* (I c).—Hydrolysis of the above ester (16 g.) with ethanolic potash (KOH 8 g., water 6 c. c. and alcohol 175 c. c.) was effected by refluxing for 13 hours in the usual way. This yielded 13.5 g. (99%) of (I c) as a colorless oil, b.p. 196-98°/6 mm. (Found : C, 77.62 ; H, 8.34. $C_{15}H_{20}O_2$ requires [C, 77.55 ; H, 8.68 per cent).

S-*Benzyl*isothiouronium *derivative* was prepared in the usual manner and crystallised from dilute alcohol, m. p. 123-24° (Found : N, 6.75. $C_{23}H_{30}O_2N_2S$ requires N, 7.03 per cent).

4-*Methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-1-*ketoanthracene* (II).—The acid (I c, 15 g.) was converted into the acid chloride with PCl_5 (14.8 g., 1 *M*) in presence of dry benzene (100 c. c.). $POCl_3$ and benzene were removed under reduced pressure. The acid chloride without being isolated was cyclised with $AlCl_3$ (8.6 g, 1.1 *M*) according to

* Melting and boiling points are uncorrected.

the conditions of Johnson (*loc. cit.*). The product (11.4 g., 83%) was obtained as a colorless oily liquid, b.p. 175-77°/10 mm. (Found: C, 83.8; H, 8.67. $C_{13}H_{18}O$ requires C, 84.07; H, 8.47 per cent).

The *semicarbazone* was prepared in the usual manner and crystallised from alcohol as colorless crystals, m.p. 203°. Mosby (*J. Org. Chem.*, 1953, **18**, 967) reports m.p. 202-203°. (Found: N, 15.9. Calc. for $C_{16}H_{21}ON_3$: N, 15.5 per cent).

The 2 : 4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and crystallised from ethyl acetate as red flakes, m.p. 208°. Mosby (*loc. cit.*) gave m.p. 209°. (Found: N, 14.1. Calc. for $C_{21}H_{22}O_4N_4$: N, 14.21 per cent).

4-*Methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene* (III).—The ketone (II, 5 g.) was reduced with amalgamated zinc (30 g.), HCl (conc., 60 c.c.), water (30 c.c.), toluene (30 c.c.) and acetic acid (1 c.c.) by refluxing for 36 hours. After every 6 hours HCl (5 c.c.) was added. The reaction mixture was worked up in the usual manner and 3.5 g. (76%) of the product (III) was obtained as a colorless oil, b.p. 162-64°/5 mm. (Found: C, 89.56; H, 9.92. $C_{15}H_{20}$ requires C, 89.94; H, 10.06 per cent).

4-*Methylanthracene* (IV).—The above product (III, 2.5 g.) was dehydrogenated with palladised charcoal (30%, 0.25 g.) at 320° by heating for 4 hours. The cooled mixture was diluted with ether and filtered. The filtrate was stripped of ether when 4-methylanthracene was obtained. It was crystallised from methanol, m.p. 85°. Brown and Bayer (*Ber.*, 1926, **59**, 914) reported m.p. 85-86°.

The picrate was prepared in the usual manner and crystallised from alcohol as red needles, m.p. 114°. Brown *et al.* (*loc. cit.*) report m.p. 113-15°. (Found: N, 9.70. Calc. for $C_{21}H_{15}O_7N_3$: N, 9.97 per cent).

5-(6′-*Tetralyl*)-*hexan*-2-*one* (I b).—Tetralin (75 c.c.) was subjected to an $AlCl_3$-catalysed reaction with allylacetone (10 g., 1 *M*) and $AlCl_3$ (20 g., 2 *M*) according to the conditions employed for (I a), and 16.9 g. (73%) of (I b) was obtained, b.p. 190-92°/9 mm. (Found: C, 83.84; H, 9.43. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63 per cent).

5-(6′-*Tetralyl*)-*hexan*-2-*ol* (V).—Ketone (I b, 6.5 g.) was reduced with sodium (5.5 g.) in moist ether. Sodium was added in small pieces gradually and whenever the reaction subsided, 1 to 2 c.c. of water was added. At the end the mixture was diluted with water and extracted with ether. After removal of the solvent, 3.5 g. (53%) of the carbinol (V) was obtained, b.p. 155-57°/4 mm. (Found: C, 83.12; H, 10.23. $C_{16}H_{24}O$ requires C, 82.7; H, 10.46 per cent).

1:4-*Dimethyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene* (VI).—The alcohol (V) was cyclised according to the method of Bogert *et al.* (*J. Org. Chem.*, 1936, **1**, 288). Treatment of the alcohol (V, 7 g.) with H_2SO_4 (conc., 7 c.c.) in the cold (0°-5°) furnished the product as a colorless mobile liquid, b. p. 146-47°/4 mm., yield 3.75 g. (60%). (Found: C, 89.44; H, 9.85. $C_{16}H_{22}$ requires C, 89.71; H, 10.3 per cent).

1:4-*Dimethylanthracene* (VII).—The product (VI, 2 g.) was dehydrogenated with Pd-C (0.2 g.) by heating to 320° for 5 hours. The dehydrogenated product was

extracted with dry ether and converted into the picrate as usual. The picrate was crystallised from alcohol as orange-red needles, m.p. 140°. Mosby (*loc. cit.*) reports m.p. 139-40°. (Found : N, 9.9. Calc. for $C_{22}H_{17}O_7N_3$: N, 9.65 per cent).

The hydrocarbon was regenerated from the picrate with dilute ammonia and crystallised from alcohol in brown needles, m.p. 73°. Mosby (*loc. cit.*) records m.p. 74°. (Found : C, 93.0 ; H, 6.85. Calc. for $C_{16}H_{14}$: C, 93.2 ; H, 6.8 per cent).

2-[*β-Methyl-β-* (6'- *tetralyl*) - *ethyl*]cyclo*hexanone* (VIII). — 2-Allylcyclohexanone (12 g.) was subjected to anhydrous $AlCl_3$-catalysed reaction with tetraline (70 c.c.) in the presence of finely powdered $AlCl_3$ (24 g.) according to the conditions employed for the preparation of (I a), when 13 g. (55%) of the ketone (VIII) boiling at 210-15°/4 mm. was obtained. (Found : C, 84.23 ; H, 9.42. $C_{19}H_{26}O$ requires C, 84.44 ; H, 9.63 per cent).

2-[*β-Methyl-β-*(6'-*tetralyl*)-*ethyl*]-cyclo*hexan*-2-*ol* (IX).—The ketone (VIII, 7 g.) in 35 c. c. of *iso*propyl alcohol was reduced with aluminium *iso*propoxide (from 2g. Al) in the usual manner. Distillation of the product under reduced pressure furnished 6.4 g. (90%) of the alcohol (IX) at 210-13°/5 mm. as a highly viscous liquid. (Found : C, 84.08 ; H, 10.45. $C_{19}H_{28}O$ requires C, 83.82 ; H, 10.28 per cent).

4-*Methyl-dodecahydro*-1 : 2-*benzanthracene* (X).—The alcohol (IX, 6 g.) was cyclised with H_2SO_4, (6 c.c., *d* 1.84) as in the case of (VI), when the hydro derivative (X) was obtained, b. p. 190-95°/6 mm., yield 5 g. (Found : C, 90.05 ; H, 9.8. $C_{19}H_{34}$ requires C, 89.70 ; H, 10.3 per cent).

4-*Methyl*-1 : 2-*benzanthracene* (XI).—The hydro derivative (X, 4 g.) was dehydrogenated with 30% Pd-C (0.4 g.) in the usual manner. After cooling, the hydrocarbon was extracted with dry ether and whole of the product was converted into the picrate. The hydrocarbon (XI) was regenerated from the purified picrate by treatment with dilute ammonia and it was crystallised from alcohol, yield 2.8 g., m.p. 121°. Cook (*J. Chem. Soc.*, 1933, 1992) records m.p. 123°. (Found : C, 93.67 ; H, 5.35, Calc. for $C_{19}H_{14}$: C, 94.2 ; H, 5.8 per cent).

The *picrate* was crystallised from alcohol as reddish brown needles, m.p. 148°. Fieser and Jones (*J. Amer. Chem. Soc.*, 1938, **60**, 1940) record m.p. 148-49°. (Found : N, 8.68. Calc. for $C_{25}H_{17}O_7N_3$: N, 8.92 per cent).

The 1 : 3 : 5-*trinitrobenzene derivative* of the hydrocarbon was prepared in the usual way and crystallised from acetic acid as red needles, m.p. 163°. Fieser and Jones (*loc. cit.*) report m.p. 163-64°. (Found : N, 9.03. Calc. for $C_{19}H_{14}.C_6H_3O_6N_3$: N, 9.30 per cent).

One of us (O.P.V) wishes to record his grateful thanks to the Ministry of Education, Govt. of India, for a Senior Research Scholarship.

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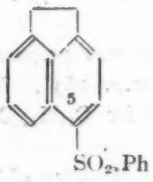
THE FRIEDEL-CRAFTS REACTION OF ACENAPHTHENE AND FLUORENE WITH ARYLSULPHONYL CHLORIDES

By Miss. A. A. Aleykutty and V. Baliah

Acenaphthene reacts with benzene- and *p*-toluenesulphonyl chloride in the presence of anhydrous stannic chloride to furnish 5-acenaphthylphenyl and 5-acenaphthyl-*p*-tolyl sulphones, respectively, in excellent yields. Fluorene reacts similarly yielding 2-fluorenylaryl sulphones. The structures of all the sulphones have been established by unequivocal syntheses.

The reaction of benzene and its derivatives with arylsulphonyl chlorides in the presence of aluminium chloride was investigated by a number of workers to prepare sulphones (Suter, "The Organic Chemistry of Sulphur", Wiley, New York, p. 675). The applicability of this reaction to polynuclear hydrocarbons has, however, not been much investigated. Beckurts and Otto (*Ber.*, 1878, **11**, 2066) reported that only a trace of a crystalline substance could be obtained from the product of reaction of benzenesulphonyl chloride with naphthalene in the presence of aluminium chloride. We have found that aluminium chloride, when used as a catalyst in the case of polynuclear hydrocarbons, generally gives rise to highly coloured products which cannot be purified easily. The use of anhydrous stannic chloride in the place of aluminium chloride afforded very satisfactory results. The yields were good and the products could be readily purified.

At 140° acenaphthene reacted with benzenesulphonyl chloride in the presence of anhydrous stannic chloride to furnish 5-acenaphthylphenyl sulphone (I) in 90% yield. The structure of the sulphone followed from the fact that it was identical with the sulphone obtained by the oxidation of 5-acenaphthylphenyl sulphide, which in turn was obtained by the condensation of 5-iodoacenaphthene and thiophenol.



(I)

(II)

Acenaphthene reacted similarly with *p*-toluenesulphonyl chloride, yielding 5-acenaphthyl-*p*-tolyl sulphone. The identity of this sulphone has also been established.

The Friedel-Crafts reaction of fluorene with benzene- and *p*-toluenesulphonyl chlorides afforded the corresponding 2-fluorenyl sulphones (II: R = Ph and *p*-tol). The structures of these sulphones were proved by preparing them from 2-fluorenesulphonyl chloride and the corresponding hydrocarbon.

EXPERIMENTAL

Preparation of 5-Acenaphthylphenyl Sulphone by the Friedel-Crafts Reaction.—A mixture of acenaphthene (3.1 g.), benzenesulphonyl chloride (3.5 g.), and anhydrous stannic chloride (8 g.) was heated gradually to 140°. There was copious evolution of hydrogen chloride. After keeping the reaction mixture at the above temperature for 10 minutes, it was cooled and treated with a 30% solution of sodium hydroxide. The solid obtained was removed by filtration, washed with water and dried. The crude product (5.3 g., 90%) was then washed with a few c. c. of ethanol. Recrystallisation from benzene-ligroin furnished needles, m.p. 184-85°. (Found : C, 73.1 ; H, 5.1. $C_{18}H_{14}O_2S$ requires C, 73.5 ; H, 4.8 per cent). The compound did not depress the melting point of a sample synthesised unequivocally (*vide infra*).

5-Acenaphthylphenyl Sulphide.—Sodium (0.46 g.) was dissolved in absolute ethanol (5 c. c.) and to the resulting sodium ethoxide was added thiophenol (2.2 g.). The alcohol was then removed by evaporation. To the dry sodium thiophenate were added 5-iodoacenaphthene (5.6 g.) (Crompton and Walker, *J. Chem. Soc.*, 1912, 963) and copper powder (0.5 g.). The mixture was heated in an oil-bath at 180°-200° for 3 hours with an air condenser. After cooling, sulphuric acid (1 : 1, 20 c.c.) and zinc dust (2 g.) were added and the unchanged thiophenol and iodoacenaphthene were removed by steam-distillation. The residual solid was extracted with ether and the ether evaporated off. The sulphide (4.5 g., 86%), after recrystallising thrice from ethanol using animal charcoal, furnished fine needles, m.p. 92-94°. (Found : C, 82.6 ; H, 5.3. $C_{18}H_{14}S$ requires C, 82.5 ; H, 5.3 per cent).

Oxidation of the foregoing sulphide in acetone with excess of hydrogen peroxide (30%) afforded 5-acenaphthylphenyl sulphone in 84% yield. The compound crystallised from benzene-ligroin as colorless needles, m. p. 185-86°. (Found : C, 73.0 ; H, 4.9. Calc. for $C_{18}H_{14}O_2S$: C, 73.5 ; H, 4.8 per cent).

Preparation of 5-Acenaphthyl-p-tolyl Sulphone by the Friedel-Crafts Reaction.—It was obtained in 88% yield from acenaphthene and *p*-toluenesulphonyl chloride by the same procedure as was used for the phenyl analogue. After recrystallising several times from toluene it melted at 185-87° with or without a sample synthesised unequivocally (*vide infra*). (Found : C, 73.5 ; H, 5.0. $C_{19}H_{16}O_2S$ requires C, 74.0 ; H, 5.2 per cent).

5-Acenaphthyl-p-tolyl sulphide was prepared in 76% yield from 5-iodoacenaphthene and *p*-thiocresol by the same procedure as was used for 5-acenaphthylphenyl sulphide. It crystallised from ethanol as fine needles, m. p. 109-10°. (Found : C, 82.2 ; H, 5.7. $C_{19}H_{16}S$ requires C, 82.6 ; H, 5.8 per cent).

The above sulphide, on oxidation in acetone with excess of hydrogen peroxide (30%), furnished 5-acenaphthyl-*p*-tolyl sulphone in 86% yield. It crystallised from acetone in colorless needles, m. p. 184-86°. (Found : C, 74.1 ; H, 5.2. Calc. for $C_{19}H_{16}O_2S$: C, 74.0 ; H, 5.2 per cent).

2-Fluorenylphenyl Sulphone.—A mixture of fluorene (3.3 g.), benzenesulphonyl chloride (3.5 g.) and anhydrous stannic chloride (8 g.) was heated in an oil-bath at 140° for 10 minutes. After cooling, it was treated with a 30% solution of sodium hydroxide,

The solid obtained was collected on a filter, washed first with water and then with a few c. c. of ethanol. The yield was 5.6 g. (92%). After crystallising from benzene, using animal charcoal, fine feathery needles melting at 198-99° were obtained. The compound did not depress the melting point (198-99°) of the sulphone obtained from 2-fluorenesulphonyl chloride (Wedekind and Stüsser, *Ber.*, 1923, **56B**, 1557) and benzene, using anhydrous aluminium chloride. (Found : C, 74.0 ; H, 4.8. $C_{19}H_{14}O_2S$ requires C, 74.5 ; H, 4.6 per cent).

2-*Fluorenyl*-p-*tolyl sulphone* was prepared in 94% yield from fluorene and *p*-toluenesulphonyl chloride in a similar manner as the preceding compound. After crystallising from toluene, using animal charcoal, colorless needles melting at 222-24° were obtained. There was no depression in melting point on admixture with the sulphone prepared from 2-fluorenesulphonyl chloride and toluene by the Friedel-Crafts reaction. (Found : C, 75.2 ; H, 5.1. $C_{20}H_{16}O_2S$ requires C, 75.0 ; H, 5.0 per cent).

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ON THE FORMATION OF COMPOUNDS IN ORGANIC SOLVENTS. PART I. REACTIONS BETWEEN SILVER IODIDE AND IODIDES OF MERCURY, CADMIUM AND ZINC

By Sarju Prasad and Prabhoo Dayal Sharma

The reaction of AgI with iodides of Hg, Cd and Zn has been studied in water, alcohol, ether, benzene, toluene, xylene and pyridine. Ag_2HgI_4, 10AgI HgI_2.13Py and CdI_2.2AgI.6Py have been isolated and their properties studied. ZnI_2 did not react with AgI in any of the solvents.

Meusel (*Ber.*, 1870, **3**, 123), Bötteger (*J. prakt. Chem.*, 1870, *ii*, **22**, 136), Bellati and Romanese, (*Atti Ist. Veneto*, 1900, **2**, 6), Steger (*Z. physikal. Chem.*, 1903, **43**, 595), Bauer (*ibid.*, 1895, **18**, 180), Crammer (*Jahrb. Phot.*, 1904, **18**, 14) and Wegelius and Kilpi (*Z. anorg. Chem.*, 1909, **61**, 413) obtained the compound Ag_2HgI_4 by different methods in aqueous medium and studied its properties such as change in colour at different temperatures, thermal expansion, specific heat, specific gravity, etc. Meusel (*loc. cit.*) and Bötteger (*loc. cit.*) regarded this compound as merely a mechanical mixture and not a definite compound. But recently Wagner and Koch (*Z. physikal. Chem.*, 1936, **33**, 309) from their studies on the reaction between AgI and HgI_2 in the solid state, concluded that a definite compound was formed by the self-diffusion of Ag^+ and Hg^{2+} ions. This was confirmed by Zimon, Johansson and Hillert (*J. Chem. Soc.*, 1949, No. 2, S 392-4).

The present authors have studied the interaction of AgI and HgI_2 in non-aqueous media by the solubility method adopted by Foote (*J. Amer. Chem. Soc.*, 1908, **30**, 330). The formation of Ag_2HgI_4 has been confirmed in all media, except in pyridine in which a different compound is formed under the same experimental conditions. The work has been extended to the study of the reaction of cadmium and zinc iodides with AgI.

Experimental

Mercury iodide and cadmium iodide of Merck's G.R. quality, zinc iodide of Merck's E.P. quality and freshly prepared AgI were used in all the experiments.

Alcohol, acetone, ether, benzene, toluene, xylene and pyridine were dehydrated and redistilled.

Procedure.—In all the sets of experiments weighed quantities of freshly prepared AgI and the other component were taken in glass-stoppered conical flasks, and a measured quantity of the liquid was added to them. The flasks were well stoppered, sealed with wax and kept in a thermostat at 30° for 48 hours with intermittent shaking. The contents were then filtered through glass wool, the residue washed once with the solvent, the filter pressed and dried in a desiccator. The residue and the filtrate were analysed separately.

Analysis.—Several methods were tried to analyse the compounds formed, but finally the Stepanov method was found to be the most suitable for the estimation

iodine, which went into solution as NaI from which it was estimated as AgI, and Ag and Hg were left as a black residue.

After washing the residue well, it was dissolved in HNO_3 (conc.), and Ag and Hg estimated in the solution in two different ways: (1) by Volhard's modified thiocyanate method as described by Caul and Shoonover (*J. Res. Nat. Bur.*, 1941, **26**, 481) and (2) by precipitating Ag as AgCl by adding dilute HCl to the solution and estimating Hg as HgS in the filtrate.

Cadmium and zinc were estimated as pyrophosphate.

AgI *and* HgI_2 *in Ethyl Alcohol and Acetone.*—AgI was taken in a fixed quantity and the proportion of HgI_2 was varied. After the equilibrium had been established it was filtered, and only the residue was analysed as the filtrate responded to no test for Ag.

TABLE I

Reaction of AgI *and* HgI_2 *in ethyl alcohol.*

Molar ratio.	Alcohol	Analysis of the residue.		Ratio of
HgI_2:AgI	added.	HgI_2.	AgI.	AgI : HgI_2.
1 :1	50 c.c.	49.46%	51.00%	2 : 1
½ :1	50	49.72	50.85	2 : 1
1½ :1	65	49.64	50.73	2 : 1
2 :1	80	49.24	50.86	2 : 1
2½ :1	100	49.32	50.00	2 : 1

The above experiments were repeated using acetone as the solvent. The empirical formula of the residue obtained corresponded to Ag_2HgI_4 in each case.

AgI *and* HgI_2 *in Water, Ether, Benzene, Toluene and Xylene.*—As both the constituents were insoluble in these liquids, a slightly modified method was followed. A weighed quantity of AgI was taken in a glass-stoppered conical flask and a slight excess of HgI_2 over that required for the formation of the compound 2AgI. HgI_2 was added to it. The compound formed was washed once with acetone, dried and analysed. All the properties of the compound formed in each case were identical with those of the compound formed in acetone or alcohol. On analysis it was found to correspond with Ag_2HgI_4.

Properties of the Compound.—The compound is bright yellow, amorphous powder. Under the ordinary and polarised light as well as under crossed-nicols of the microscope the colour remains yellow of the III order. It is insoluble in water, alkalies and in dilute or strong acids except in boiling aqua regia. It does not melt but decomposes when heated. It is yellow in all the solvents at the ordinary temperature but changes to red on warming and yellow on cooling again, but with no sharp transition. The compound, when heated with acetone or alcohol, slowly decomposes, which, however, does not take place if any of the components is in excess. The formation of the compound in organic solvents and in water, in which both the components are insoluble, shows that the reaction proceeds through the diffusion of Ag^+ and Hg^{2+} ions, as has been observed by Wagner *et al.* (*loc. cit.*).

The change in colour appears to be due to dimorphism (cf. Wegelius, *Z. anorg. Chem.*, 1911, **77**, 587) and not due to the decomposition (cf. Bauer, *loc.cit.*) which has been confirmed by the following experiment.

A saturated solution of HgI_2 in acetone was taken in a glass-stoppered conical flask and an excess of AgI added to it. It was left in a thermostat at 30° for 48 hours. It was then heated at 50° for half an hour and filtered hot through glass wool in a weighed dish. The filtrate on evaporation left only traces of HgI_2, indicating that all the HgI_2 had been utilised in the formation of the compound and the traces obtained were due to slight decomposition through boiling with acetone.

No compound of AgI was formed with CdI_2 or ZnI_2 in the solvents mentioned above.

Formation of the Compound of AgI *with* HgI_2, CdI_2 *or* ZnI_2 *in Pyridine*

AgI and the other components were dissolved separately in pyridine by gently warming them. The two solutions were mixed together and concentrated on a water-bath when a crystalline transparent compound separated out, which dissolved when the solution was cooled to the room temperature. The mixture was heated on the water-bath when the substance separated out again. It was filtered through a stoppered Gooch crucible, washed once with hot pyridine, the filter pressed and kept in a desiccator.

HgI_2 *and* AgI.—A crystalline transparent compound, turning opaque on exposure to atmosphere, was obtained. The empirical formula from the results of two analyses was found to be $10AgI.HgI_2.13$ Py (Py stands for pyridine). [Found: Ag, 27.95; Hg, 5.22; I, 40.04; Py (by diff.), 26.79. $10AgI.HgI_2.13Py$ requires Ag, 28.18; Hg, 5.22; I, 39.78; Py, 26.32 per cent].

On exposure to the atmosphere it changed colour from pale yellow to orange. This change in colour seems to be due to the loss of pyridine. It was confirmed by heating the compound at 60° in an air-oven and noting the loss in weight and the change in colour. The loss of pyridine was regular in the beginning but after 7½ hours' heating the remaining pyridine was lost in a much shorter duration and the resulting compound became orange in colour.

CdI_2 *and* AgI.—A transparent crystalline compound, turning yellowish on exposure to atmosphere, was formed. The compound was analysed. [Found: Cd, 10.6; Ag, 10.00; I, 35.98; Py (by diff.), 43.42. $CdI_2.AgI.6Py$ requires Cd, 10.45; Ag, 10.03; I, 36.22; Py, 43.37 per cent]. This compound is fairly stable and does not lose pyridine so readily as the mercury compound.

ZnI_2 *and* AgI.—A white crystalline compound, which turned pinkish, was formed. The compound was analysed. [Found: Zn, 13.52; I, 53.3; Py (by diff.), 33.18. $ZnI_2.2$ Py requires Zn, 13.7; I, 53.18; Py, 33.12 per cent]. AgI did not form a compound with ZnI_2 in pyridine.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS: OXIDATION WITH POTASSIUM IODATE

By S. M. A. Azim and Ahsanulhaq Rehman

Mercurous chloride, antimony trichloride, arsenious oxide and stannous chloride have been determined potentiometrically by using potassium iodate, in presence of hydrochloric acid, as the oxidising agent at 15°, using a platinum electrode coupled with a saturated calomel electrode.

The potentiometric method for the determination of end-point with potassium iodate in the presence of hydrochloric acid has been applied by Kolthoff (*Rec. trav. chim.*, 1920, **39**, 212) for the estimation of iodide. Fenwick (Dessert. Ann. Arbor., 1922, p. 76) and Hendrixson (*J. Amer. Chem. Soc.*, 1925, **47**, 1319) used it as a potentiometric reagent for the estimation of thiocyanate and sulphite ions, respectively. One of us (Singh and Rehman, this *Journal*, 1942, **19**, 349) used potassium iodate and concentrated hydrochloric acid as chlorinating agent for the estimation of aromatic amines by the potentiometric method. In the present investigation, potentiometric determinations of mercurous chloride, antimony trichloride, arsenious oxide and stannous chloride have been carried out with potassium iodate as the oxidising agent.

Potassium iodate reacts with potassium iodide in acid solution to liberate iodine, thus:

$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O.$$

But Andrews (*J. Amer. Chem. Soc.*, 1903, **25**, 756; *Analyst*, 1903, **28**, 306) has shown that in the presence of sufficient concentrated hydrochloric acid the reaction proceeds thus:

$$KIO_3 + 2KI + 6HCl = 3KCl + 3ICl + 3H_2O.$$

One molecule of iodate oxidises only two molecules of iodide and not five, as in the first reaction. In this and similar titrations with iodate, it is essential that the acidity of the solution at the end of the titration should not be less than 3 *N* and not more than 5*N*. Too little acidity fails to prevent hydrolysis of ICl owing to disturbance of the equilibrium:

$$ICl + H_2O \rightleftharpoons HCl + HIO,$$

while with an excess the reaction takes place too slowly.

Fenwick (*loc. cit.*) applied the Andrews method (*loc. cit.*) for the potentiometric determination of thiocyanate with potassium iodate.

Potassium iodate oxidises mercurous chloride, antimony trichloride, arsenious oxide and stannous chloride according to the following equations:

1. $2Hg_2Cl_2 + KIO_3 + 6HCl = 4HgCl_2 + KCl + ICl + 3H_2O$
2. $2SbCl_3 + KIO_3 + 6HCl = 2SbCl_5 + KCl + ICl + 3H_2O$
3. $As_2O_3 + KIO_3 + 2HCl = As_2O_5 + KCl + ICl + H_2O$
4. $2SnCl_2 + KIO_3 + 6HCl = 2SnCl_4 + KCl + ICl + 3H_2O$

These reactions have been utilised in the quantitative determination of these substances by the potentiometric method.

EXPERIMENTAL

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in the solution to be titrated, was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water-bath, maintained at 15°. E. M. F. of the cell was read on a potentiometer.

A known weight of the substance was mixed with water and acidified with the requisite amount of HCl (conc.) and titrated potentiometrically against standard potassium iodate. The mixture was kept stirred thoroughly with a mechanical stirrer.

The potentiometric readings were recorded after the addition of the reagent, when the potential acquired a steady value. A series of potentiometric titrations were performed with different amounts of each substance. One titration as typical of the set is recorded below.

TABLE I

Titration of 0.1778 *g. of arsenious oxide mixed with* 20 *ml. of water & conc.* HCl *against* $M/20$-KIO_3.

KIO_3.	E.M.F.	*E/C.*	KIO_3.	E.M.F.	*E/C.*	KIO_3.	E.M.F.	*E/C.*	KIO_3.	E.M.F.	*E/C.*
0.00 ml.	396 mv		15.00 ml.	587 mv		17.70 ml.	670 mv		18.50 ml.	881 mv	
		29			27			90			28
4.00	500		16.00	604		17.80	679		19.00	895	
		4			33			160			16
7.00	512		16.60	623		17.85	687		20.00	911	
		6			40			420			14
9.00	524		17.00	633		17.90	708		21.00	925	
		8			47			2140			11
11.00	530		17.30	647		17.95	815	(max.)	23.00	947	
		11			50			380			7
13.00	552		17.50	657		18.00	834		25.00	960	
		14			60			140			4
14.00	566		17.60	663		18.10	848		28.00	971	
		21			70		82				

These titrations showed that with the addition of standard potassium iodate solution, the E. M. F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential, followed by a steady rise, with the further addition of the reagent.

From the volume of potassium iodate required in each titration, corresponding to the equivalence point, the amount of each compound was calculated. The following table records the values obtained which have been compared with the amounts of the substances taken.

TABLE II

Mercurous chloride.		Antimony trichloride.		Arsenious oxide.		Stannous chloride.	
Taken.	Found.	Taken.	Found.	Taken.	Found.	Taken.	Found
0.2594 g.	0.2597 g.	0.2855 g.	0.2851 g.	0.1778 g.	0.1775 g.	0.3548 g.	0.3543 g.
0.3772	0.3766	0.4110	0.4106	0.1976	0.1978	0.5693	0.5686
0.4324	0.4321	0.4761	0.4768	0.2965	0.2967	0.7372	0.7379
0.7092	0.7083	0.7185	0.7187	0.3955	0.3946	0.9133	0 9139
0.9449	0.9444	0.9405	0.9399	0.4971	0.4 65	1.1314	1.1305

These results show that mercurous chloride, antimony trichloride, arsenious oxide and stannous chloride can be determined potentiometrically by using potassium iodate in presence of hydrochloric acid, as the oxidising agent.

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FRIEDEL-CRAFTS REACTION INVOLVING UNSATURATED KETONES AND ESTERS. PART IV. THE STUDY OF THE FRIEDEL-CRAFTS REACTION BETWEEN METHYLHEPTENONE AND TOLUENE

By Naba Kumar Bhattacharyya *

6-Methyl-6-*m*-tolylheptan-1-one (I) has been synthesised by the application of the Friedel-Crafts reaction with toluene and methylheptenone. (I) on oxidation with alkaline permanganate furnishes αα-dimethylhomo*iso*phthalic acid, and on reduction with Na in moist ether, the carbinol (V). The latter on treatment with H_2SO_4 (conc.) leads to a hydrocarbon, which on sulphur dehydrogenation yields a naphthalene derivative.

With a view to synthesising some polyalkylated naphthalene derivatives through the application of the Friedel-Crafts reaction with aromatic compounds and unsaturated aliphatic ketones and esters, investigations have been carried out using toluene and methylheptenone. That the Friedel-Crafts reaction may lead, as the major product, to the *meta*-oriented derivatives with reference to the methyl group of the toluene nucleus, has been definitely proved by a number of observations (Baddeley, *J. Chem. Soc.*, 1935, 303 ; Nightingale, *Chem. Rev.*, 1939, **25**, 354 ; Norris and Rubinstein, *J. Amer. Chem. Soc.*, 1939, **61**, 1163 ; Bhattacharyya *et al.*, *J. Org. Chem.*, 1953, **18**, 1499 ; Chowdhury, *Science & Culture*, 1953, **19**, 442). In the present investigation, it has been found that the condensation goes well at a low temperature. The saturated ketone (I) has been isolated in a very good yield ; it has been characterised by a well-defined semicarbazone. As expected, the attack on the methylheptyl residue has been through the tertiary carbon atom involved in the unsaturated linkage (cf. Bruson and Kroeger, *J. Amer. Chem. Soc.*, 1940, **62**, 36). To prove the structure of the condensation product (I), it has been oxidised with an excess of alkaline potassium permanganate. A dibasic acid of m.p. 167-68° has been isolated and identified with αα-dimethylhomo*iso*phthalic acid (IV), an authentic sample of which has been synthesised by the following method.

3-Methyl-Δ^2-*cyclo*hexenone is condensed with ethyl α-bromopropionate by Reformatsky's reaction and the resulting product on dehydration and dehydrogenation with sulphur leads to (II). The corresponding acid is methylated with excess of potassium and methyl iodide in liquid ammonia to form (III), which, in its turn, on oxidation with potassium permanganate furnishes (IV) in a very good yield. It may be mentioned that during the process of isolation of (IV) from the oxidation of (I), small amounts of two isomeric acids, melting at 114° and 225°, have been isolated. The former one may correspond to the *ortho*-isomer, αα-dimethylhomophthalic acid (Anchel and Blatt, *J. Amer. Chem. Soc.*, 1941, **63**, 1948) and the latter one is most probably the corresponding *para*-isomer, αα-dimethylhomoterephthalic acid (Colongi and Pichat, *Bull. soc. chim.*, 1949, 177). This shows that the original condensation product (I) is probably a mixture of all the three possible isomers. But the close proximity of

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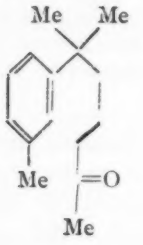
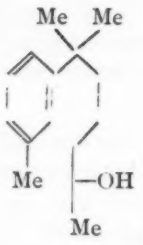
the melting point, 155-58°, of the crude oxidation product with that of (IV) and also the yield of the pure semicarbazone, described before, support the fact that the condensation has mostly taken place in the *meta*-position of the toluene nucleus.

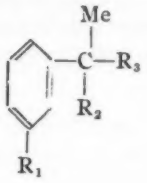
The ketone (I), purified through its semicarbazone, is reduced with sodium in moist ether to the carbinol (V). This on treatment with concentrated sulphuric acid leads to a hydrocarbon, which on dehydrogenation with sulphur yields a naphthalene derivative. This has been characterised by a red picrate, melting at 135-36°. Investigations are in progress to determine the structure of this naphthalene derivative.



(I)



(V)



II : $R_1 = Me$, $R_2 = H$, $R_3 = CO_2Et$.
III : $R_1 = R_2 = Me$, $R_3 = CO_2Et$.
IV : $R_1 = R_3 = CO_2H$, $R_2 = Me$.

EXPERIMENTAL

6-Methyl-6-m-tolylheptan-2-one (I).—Anhydrous aluminium chloride (21 g.) and freshly distilled methylheptenone (12.6 g.) were added alternately, within 45 minutes, to a vigorously stirred, dry, purified toluene (46 c.c.), kept at 0°-5°. The temperature rapidly rose to 25°-30°, which was brought down quickly by efficient cooling. Stirring was continued for 2 hours more. This was then decomposed with iced HCl, maintaining the inside temperature within 5°-15°, and worked up as usual (Bhattacharyya *et al*, *loc.cit.*). The residue left after evaporation of the solvent afforded a clear colorless liquid, b.p. 136-37°/3-4 mm., yield 15.7 g. (72%). (Found: C, 82.84; H, 10.28. $C_{15}H_{22}O$ requires C, 82.57 ; H, 10.09 per cent).

The *semicarbazone* was prepared in the usual way in a quantitative yield (crude, m.p. 120-22°) and recrystallised from ethanol (60%) as a fine white solid, m.p. 124-25°. Further crystallisation failed to raise the m. p. (Found: C, 69.62 ; H, 9.47. $C_{16}H_{25}ON_3$ requires C, 69.82 ; H, 9.09 per cent).

αα-Dimethylhomoisophthalic Acid (IV).—The above ketone (I, 2 g.) was oxidised with alkaline potassium permanganate (17 g., water 500 c c., NaOH 32 g.) at 120°-140° with mechanical stirring for 7 hours. The excess of permanganate was destroyed with alcohol. The clear filtrate was once washed with ether and concentrated to a suitable volume on a water-bath. The concentrate was cooled in an ice-bath and slowly acidified with HCl (conc.). The separated acid was filtered off and the mother-liquor was extracted four times with ether. The ethereal solution was dried (Na_2SO_4) and evaporated to dryness. The solid residue and the separated solid (crude, m.p. 155-58°) were mixed up and sublimed at 140°-160°/2 mm., when at first a very small amount of fine, white,

needle-like substance came out, m.p. 116-18°. This was removed and on crystallisation from concentrated aqueous solution it melted at 114°. This corresponded to the *ortho*-isomer (lit. m. p. 114°). Sublimation was again continued, when a white mass sublimed over, m.p. 159-60°. This was recrystallised from an ether-benzene mixture to a constant melting solid, m.p. 167-68° which remained undepressed when mixed with the authentic sample of αα-dimethylhomo*iso*phthalic acid (*vide infra*). (Found : C, 63.31 ; H, 5.92. $C_{11}H_{12}O_4$ requires C, 63.46; H, 5.77 per cent).

A small insoluble residue, left in the filter paper during crystallisation, melted at 225°, which may be αα-dimethylhomoterephthalic acid (lit. m.p. 223-24°).

Dimethyl Ester of the Crude Acid Mixture.—The crude acid (m.p. 155-58°, 3 g.) was treated with excess of diazomethane in ethereal solution. The excess of diazomethane and ether was evaporated off and the product was distilled in vacuo, when a clear liquid, b.p. 135-37°/3-4 mm., came over quantitatively. (Found : C, 65.95 ; H, 7.0. $C_{13}H_{16}O_4$ requires C, 66.10 ; H, 6.78 per cent).

6-*Methyl*-6-m-*tolylheptan*-2-*ol* (V).—The ketone (I, 8.17 g.), purified through semicarbazone, was reduced with sodium (2.3 g.) in moist ether (water 8.3 c.c., ether 40 c.c.) and worked up as usual. Distillation of the residue, obtained after removal of the ether, yielded a colorless mobile oil (7.6 g.), b.p. 141-42°/3-4 mm., yield 90-91%. (Found : C, 81.40 ; H, 10.98. $C_{15}H_{24}O$ requires C, 81.81 ; H, 10.91 per cent).

Ethyl α-*Methyl*-m-*tolylacetate* (II).—The Reformatsky reaction with 3-methyl-*cyclo*hexenone (16.5 g.), ethyl α-bromopropionate (54.3 g.) and zinc (19.5 g.) in dry benzene (200 c.c) was carried out as usual. 3-Methyl*cyclo*hexenone was prepared through the Birch reduction of *meta*-cresol methyl ether. On distillation a colorless liquid, b.p. 102-103°/3 mm., came over, yield 20 g. (65%). The above hydroxy compound (20 g.) was dehydrated with pyridine (15 g.) and thionyl chloride (14 g.) in dry benzene (100 c.c.) in the usual manner. The oil (16.0 g.), obtained by distillation in vacuo, b.p. 85°-115°/5-6 mm., was taken in a Claisen flask having its side-arm closed and fitted with an air condenser and heated with finely powdered sulphur (2.4 g.) at 160°-225° for 1¾ hours, and directly distilled under vacuum, when a clear liquid, b.p. 105-108°/3-4 mm., was obtained, yield 12 5 g. (65%). (Found : C, 75.3 ; H, 8.6. $C_{12}H_{16}O_2$ requires C, 75.0 ; H, 8.3 per cent).

αα-*Dimethyl*-m-*tolylacetic Acid* (III).—The ester (II, 12 g.) was hydrolysed with alcoholic alkali (KOH 10.5 g., water 10 c.c., rectified spirit 120 c.c.) by refluxing for 6 hours and worked up in the usual way. On distillation of the residue, left after removal of the ether, a pale yellow slightly viscous liquid, b.p. 135°-140°/3-4 mm., was obtained, yield 9.1 g. (91-92%). Liquid ammonia (500 c c.) was taken in a three-necked flask (2 lit.) fitted with a mechanical stirrer, a guard tube (KOH) and a dropping funnel. Clean potassium (8.5 g.) was added with stirring within 15 minutes, and after 10 minutes two or three crystals of ferric nitrate were added to it when the blue colour changed to brown. After 45 minutes, the above acid (8.5 g.) in dry ether (50 c.c.) was slowly added when the colour changed to reddish brown. Stirring was continued, and after 10 minutes methyl iodide (35-40 g.) was added and stirred until nearly the whole of ammonia evaporated off. This was slowly decomposed with dilute HCl (tested with Congo-red paper)

and the separated solid was filtered off. The crude product melted at 60-65°, yield 9.5 g. (96-97%). This was soluble in almost all solvents and finally it was crystallised from ethyl acetate in the cold in beautiful hexagonal crystals, m.p. 78-79°. (Found : C, 74.5 ; H, 8.1. $C_{11}H_{14}O_2$ requires C, 74.2 ; H, 7.9 per cent).

αα-Dimethylhomoisophthalic Acid (VI).—The acid (III, 4.45 g.) was oxidised with $KMnO_4$ (7.9 g., NaOH 14 g. and water 200 c.c.) at 120°-140°, as described before, and the clear filtrate on acidification furnished a milky white solid acid. This was filtered off, m.p. 167-68°, yield 4.5 g. (almost quantitative). This was recrystallised from boiling water twice, m.p. 168-69°. (Found : C, 63.46 ; H, 5.89. $C_{11}H_{12}O_4$ requires C, 63.46 ; H, 5.77 per cent).

Thanks are due to Dr. P. C. Dutta for his kind help during the course of these investigations.

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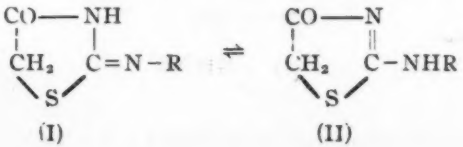
MERCURATED DERIVATIVES OF 2-ARYLIMINO-4-THIAZOLIDONES

By G. N. Mohapatra and M. K. Rout

Fifteen substituted 2-aryl (phenyl, *o*-, *m*-, *p*-tolyl; *o*-, *m*-, *p*-nitrophenyl; *o*-, *m*-, *p*-chlorophenyl; *o*-, *m*-, *p*-carboxyphenyl; α- and β-naphthyl)-imino-4-thiazolidones have been mercurated with mercuric acetate, and their corresponding chloro- and bromo-mercuri derivatives have also been prepared. The mercurated compounds have been tested against certain pathogenic bacteria and test fungus with promising results.

In view of the importance of thiazolidone compounds in medicine (Surrey, *J. Amer. Chem. Soc.*, 1949, **71**, 3354; Troutman and Long, *ibid.*, 1948, **70**, 3436; Surrey and Cutler, *ibid.*, 1954, **76**, 578) and the pronounced antibacterial action of organomercurials (Guha Sircar and Rout, this *Journal*, 1953, **30**, 359; Pujari and Rout, *J. Amer. Chem. Soc.*, 1953, **75**, 4057), it was considered worthwhile to prepare some mercurated thiazolidones and test them against certain pathogenic bacteria. Again, the pronounced activity of some thiazole compounds (Dimond and Horsfall, *Science*, 1943, **97**, 144; *Phytopath.*, 1944, **34**, 136; Mohapatra and Rout, this *Journal*, 1955, **32**, 55; *Nature*, 1954, **174**, 518) and rhodanine (Bradsher *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 114) as fungicides and the commercial use of some organo-mercurials against plant diseases, caused by certain fungi, led us to study also the fungicidal action of the above mercurated thiazolidones.

In the present investigation, fifteen different 2-substituted-arylimino-4-thiazolidones, prepared by us earlier, have been mercurated using mercuric acetate to furnish acetoxymercuri compounds in which the acetoxymercuri group is assumed to have entered the aryl nucleus attached to the imino group. This assumption finds justification from the observation that 2-imino-4-thiazolidone, which does not contain an aryl nucleus attached to the imino group, does not undergo mercuration under the present experimental conditions. The possibility of acetoxymercuri group being linked to the active $-CH_2$ group in the 5-position is excluded, since 2-arylimino-5-arylidene-4-thiazolidone, obtained by condensing 2-arylimino-4-thiazolidone with aromatic aldehydes, and 5:5-dimethyl-2-arylimino-4-thiazolidone (prepared from bromo*iso*butyric acid) could be mercurated as smoothly as the parent substance. Mercury has not entered -NH group in 3-position, forming N-acetoxymercuri compound, as the compound in that case could be very easily decomposed by alkali. The thiazolidone compound (I) can isomerise easily to its tautomeric form (II), and the resulting -NH group in position-2 would clearly be capable of orienting the incoming acetoxymercuri group to its *ortho* or *para* position on the basis of the observations made earlier on the mercuration of aromatic amines and phenols (Friend, "Text Book of Inorganic Chemistry", Vol. XI, Part I, 1928; Guha Sircar and Rout, this *Journal*, 1952, **29**, 779).



(I) (II)

These acetoxymercuri compounds have been converted into chloro- and bromo-mercuri compounds, since a few of the former compounds were found earlier by Guha Sircar *et al.* (*ibid.*, 1951, **28**, 80 ; 1953, **30**, 359) to be more effective antibacterials than the corresponding acetoxymercuri compounds.

Chloromercuri compounds have been prepared in various ways by different workers, one of the methods used being addition of a concentrated solution of acetoxymercuri compound in acetic acid to a solution of sodium chloride. As the acetoxymercuri compound is sparingly soluble in acetic acid, this method has not been used and the chloromercuri compounds have been prepared by Bruice's method (*J. Amer. Chem. Soc.*, 1950, **72**, 598). The method consists in adding sodium chloride to the reaction mixture from which the acetoxymercuri compound is to be isolated, and it thus differs from the usual procedure of isolating the acetoxymercuri compounds and then adding sodium chloride to its acetic acid solution.

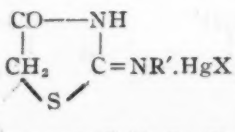
Bromomercuri compounds have been prepared in a similar way by adding a concentrated solution of sodium bromide to the reaction mixture from which the acetoxymercuri compound is to be isolated.

The Rideal-Walker drop dilution method was used for assaying the antibacterial action of the acetoxy-, chloro- and bromo-mercuri compounds. The test organisms were 24 hours' cultures of *E. Coli and Staphylococcus aureus*. The antibacterial data confirm the earlier conclusion that introduction of Hg enhances the bactericidal activity considerably. While the unmercurated compounds are active only in miximum dilutions of 1 : 200, some of the mercurated compounds containing acetoxymercuri group show activities in dilutions up to 1 : 40,000. Chloro and bromo-mercuri compounds are active in the same range of dilutions or slightly more. The antibacterial data are shown in Table II.

For assaying fungicidal activity, the method of Montgomery and Moore (*J. Pomol. & Hort. Sci.*, 1938, **15**, 253) with slight modifications was used. *Alternaria palanduii* Ayyangar was used as the test fungus. The compounds were found to possess appreciable fungicidal activity, the percentage of inhibition of spore germination being cent per cent at 50 p.p.m in case of thiazolidone compounds and at 5-6 p.p.m with the acetoxy- and chloro- and bromo-mercuri compounds. Details of the fungicidal tests will be published elsewhere.

EXPERIMENTAL

The experimental procedure adopted for the preparation of acetoxy-, chloro- and bromo-mercuri compounds (III) has been illustrated in one of each class.



[III : R = various substituents as in Table I ; X = $MeCO_2$, Cl or Br]

TABLE I

2-(Acetoxy- or chloro- or bromo-mercuri)-arylimino-4-thiazolidones.

Compound No.	Substituent R′.	Acetoxymercuri Comp.				Chloromercuri Comp.				Bromomercuri Comp.			
		*M.P.	Yield.	% Hg. Found.	% Hg. Calc.	M.P.*	Yield.	% Hg. Found.	% Hg. Calc.	M.P.*	Yield.	% Hg. Found.	% Hg. Calc.
1	-C_6H_4-	220°	70%	43.85	44.44	345°(d)	75%	46.41	46.89	280°	76%	41.78	42.46
2	-(*o*)-$C_6H_3(CH_3)$-	185°	75	43.53	43.10	315°	72	44.75	45.40	>350° (only softons & decomp.)	67	40.75	41.23
3	-(*m*)-$C_6H_3(CH_3)$-	192°	78	42.83	43.10	350°(d)	78	45.11	45.40	276°	65	41.53	41.23
4	-(*p*)-$C_6H_3(CH_3)$-	211°	80	42.75	43.10	260°	73	45.61	45.40	>350° (only softens)	69	41.03	41.23
5	-(*o*)-$C_6H_3(NO_2)$-	220°	65	40.85	40.40	195°	55	41.92	42.41	>350° (only softens)	50	38.15	38.76
6	-(*m*)-$C_6H_3(NO_2)$-	190°	60	40.15	40.40	212°	59	42.65	42.41	165°	55	37.97	38.76
7	-(*p*)-$C_6H_3(NO_2)$-	206°	68	39.85	40.40	242°	63	41.75	42.41	198°	57	37.86	38.76
8	-(*o*)-$C_6H_3(Cl)$-	207°	75	40.78	41.28	>350°(d)	75	42.78	43.38	180°	71	38.83	39.56
9	-(*m*)-$C_6H_3(Cl)$-	178°	70	41.77	41.28	180°	80	42.92	43.38	260°(d)	76	38.99	39.56
10	-(*p*)-$C_6H_3(Cl)$-	150°	80	41.60	41.28	170°	78	43.35	43.38	>350°(d) (only softens)	80	39.06	39.56
11	-(*o*)-$C_6H_3(COOH)$-	240°	50	40.53	40.49	345°(d)	56	41.75	42.50	>350°(d) (only softens)	55	38.15	38.83
12	-(*m*)-$C_6H_3(COOH)$-	263°	55	40.78	40.49	280°(d)	60	41.87	42.50	278°(d)	58	38.35	38.83
13	-(*p*)-$C_6H_3(COOH)$-	>350° (only softens)	58	39.64	40.49	290°(d)	63	41.95	42.50	290°(d)	60	37.93	38.83
14	-(α)-$C_{10}H_6$-	170°	80	39.35	40.00	325°(d)	90	40.99	41.98	323°(d)	85	38.52	38.39
15	-(β)-$C_{10}H_6$-	226°	85	39.85	40.00	257°(d)	85	41.56	41.98	335°(d)	91	37.56	38.39

* All the melting points were taken on the Gallenkamp electrically heated metallic melting point apparatus

2-p-*Acetoxymercuriphenylimino-4-thiazolidone.*—2-Phenylimino-4-thiazolidone (1 g.) was dissolved in alcohol-dilute acetic acid solution and was then treated with an aqueous solution of mercuric acetate (2 g. in 30 c.c. of water), acidified with acetic acid. There was precipitation after sometime. The reaction mixture was kept overnight. The precipitate was collected and was washed repeatedly with hot water and finally with alcohol and very dilute acetic acid.

2-p-*Chloromercuriphenylimino-4-thiazolidone.*—Acetic acid (4.8 g.) was treated with $NaHCO_3$ (2.5 g.) and diluted with 30 c.c. of water (p_H 4.3) and to that mercuric acetate (3.2 g.) was added, followed by 0.8 g. of 2-phenylimino-4-thiazolidone, dissolved in alcohol-dilute acetic acid solution. On addition of a concentrated solution of sodium chloride (2.5 g. in 10 c.c. of water), a white precipitate appeared. The reaction mixture after setting aside for 24 hours was filtered and then washed thoroughly with water, followed by alcohol.

2-p-*Bromomercuriphenylimino-4-thiazolidone.*—The method was exactly the same as above, the only difference being that concentrated NaBr solution was added instead of NaCl. The properties and analytical data of the resulting mercurated thiazolidones are shown in Table I.

TABLE II

Antibacterial data of 2-(p-acetoxy- or chloro- or bromo-mercuri)-arylimino-4-thiazolidones.
[M.E.D. for unmercurated thiazolidones against *E. Coli* and *Staph. aureus* = 1:200].

*No of compounds.	Acetoxymercuri. M.E.D.		Chloromercuri M.E.D.		Bromomercuri. M.E.D.	
	E. Coli.	*Staph. aur.*	*E. Coli*	*Staph. aur.*	*E. Coli.*	*Staph. aur.*
1	1:20,000	1:20,000	1:20,000	1:20,000	1:80,000	1:80,000
2	1:20,000	1:20,000	1:50,000	1:50,000	1:100,000	1:40,000
3	1:20,000	1:40,000	1:80,000	1:80,000	1:40,000	1:40,000
4	1:20,000	1:20,000	1:80,000	1:40,000	1:10,000	1:10,000
5	1:10,000	1:10,000	1:10,000	1:10,000	1:10,000	1:10,000
6	1:10,000	1:10,000	1:10,000	1:10,000	1:10,000	1:10,000
7	1:10,000	1:10,000	1:10,000	1:10,000	1:20,000	1:10,000
8	1:20,000	1:10,000	1:40,000	1:80,000	1:40,000	1:40,000
9	1:40,000	1:20,000	1:40,000	1:40,000	1:40,000	1:40,000
10	1:40,000	1:40,000	1:40,000	1:80,000	1:40,000	1:10,000
11	1:20,000	1:20,000	1:10,000	1:10,000	1:10,000	1:10,000
12	1:20,000	1:20,000	1:20,000	1:20,000	1:10,000	1:10,000
13	1:20,000	1:10,000	1:40,000	1:20,000	1:10,000	1:10,000
14	1:40,000	1:40,000	1:40,000	1:20,000	1:40,000	1:40,000
15	1:40,000	1:20,000	1:40,000	1:20,000	1:80,000	1:80,000

* These numbers refer to compounds bearing same numbers in Table I

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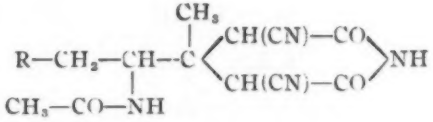
ON THE SYNTHESIS OF Δ^1-PYRROLINE DERIVATIVES. PART I

By T. N. Ghosh and Saktipada Dutta

In contrast with the usual formation of the Guareschi imides when ketones are allowed to react in presence of ammonia with ethyl cyanoacetate or its amide, an α-acetamidoketone under similar condition has been found to furnish a compound, possibly represented by the aminopyrroline structure (X). The mechanism suggested for its production is based on the initial formation of a carbinol-amine which then reacts with cyanoacetamide (cf. Robinson, *J. Chem. Soc.*, 1917, **111**, 876) and the resulting intermediate readily cyclises, under the experimental condition, to form (X).

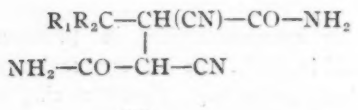
Ketones condense with ethyl cyanoacetate or cyanoacetamide in presence of ammonia to cyclic imides, known as "Guareschi imides". In an approach towards the synthesis of *iso*quinolines having a strong basic group (*e.g.*, piperidine ring) at the 3-position as possible antispasmodics, α-acetamidoketones have been allowed to react in the cold with ethyl cyanoacetate in presence of alcoholic ammonia, so that the corresponding cyclic imide (I), if formed, could be possibly utilised as a starting material for the synthesis of the above type of *iso*quinoline derivatives.



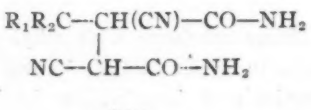
(I: R = phenyl or substituted phenyl)

However, it is of interest to record that the reaction has furnished an amine (designated A) which is soluble in cold dilute hydrochloric acid and insoluble in alkali and is unaffected by boiling with dilute hydrochloric acid. It slowly turns brown in the air, affords a stable picrate, a Schiff's base with benzaldehyde and readily forms in aqueous suspension an acetyl derivative (insoluble in alkali) and condenses with *iso*thiocyanate to yield the corresponding thiocarbamide derivative. The acetyl derivative shows feeble basicity in that it furnishes an unstable hydrochloride which gradually loses hydrochloric acid on standing at room temperature. No such amine is formed if the relevant α-acetamidoketone is allowed to stand in presence of alcoholic ammonia alone, but requires the presence of ethyl cyanoacetate as well. It is significant to observe that the same amine is obtained if cyanoacetamide is used in place of ethyl cyanoacetate. This shows that probably the latter is first converted into the former which, in its turn, takes part in the reaction with α-acetamidoketone in presence of ammonia.

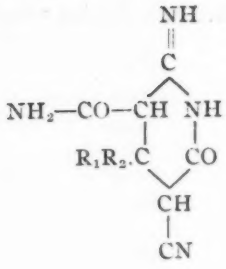
Ketones react with cyanoacetamide in presence of piperidine to furnish the six-membered cyclic compounds, (IV) and (V). Compound (IV) is formed by *trans*-addition and predominates, while compound (V) is formed by *cis*-addition. In the presence of ammonia the second type of product is solely formed (cf. Thorpe and Wood, *J. Chem. Soc.*, 1913, **103**, 1586; Kon and Thorpe, *ibid.*, 1919, **115**, 686). In fact, it has been found that unless cyanoacetamide is freed from the last traces of ammonia used in its preparation, no condensation base could be formed from it. In the first stage of the reaction an unsaturated amide, $R_1R_2C = C(CN)—CO—NH_2$, is formed which reacts with another molecule of cyanoacetamide to form the compounds, (II) and (III), which then cyclise to (IV) and (V) respectively. While (V) is acidic in nature, (IV) possesses both acidic and basic properties, being soluble in cold dilute alkali and in dilute hydrochloric acid. Further, the compound (IV) is readily hydrolysed by boiling with dilute hydrochloric acid to the cyclic imide (VI).



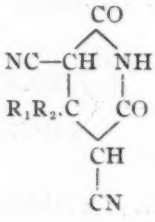
(II)



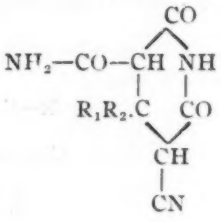
(III)



(IV)

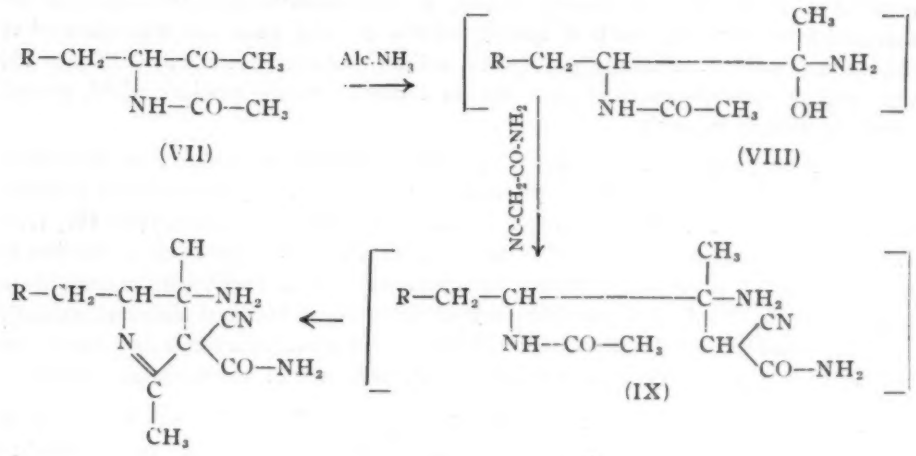


(V)

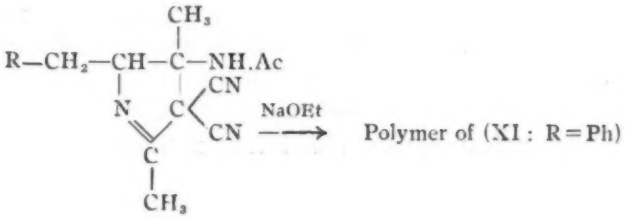


(VI)

Comparison of the properties of (IV) and (V) with those of (A) would show that (A) cannot have a structure of the type (IV) or (V), and it is therefore apparent that the reaction of an α-acetamidoketone with cyanoacetamide in presence of ammonia is taking a different course The properties of (A), coupled with the analytical data, tend to suggest that probably the reaction is taking the following course : the α-acetamidoketone (VII) forms the corresponding carbinol-amine (VIII) (cf. Wallach, *Annalen*, 1905, **343**, 54; Robinson, *J. Chem. Soc.*, 1917, **111**, 876) which then reacts with cyanoacetamide in alkaline medium (cf. Higson and Thorpe, *J. Chem. Soc.*, 1906, **89**, 1455) and the hypothetical intermediate cyano compound (IX) readily cyclises, under the experimental condition, to yield the Δ^1-pyrroline derivative (X).



[X: R = Ph, *p*-Cl-C_6H_4, *p*-NO_2-C_6H_4]



(XI : R = Ph)

Regarding the elaboration of the methods of preparation of Δ^1-pyrrolines, reference may be made to the synthesis of 2-phenylpyrroline by Cloke (*J. Amer. Chem. Soc.*, 1929, **51**, 1174) by the action of magnesiumphenyl bromide on γ-chlorobutyronitrile. The reaction has been subsequently utilised by Cloke and his co-workers for the synthesis of a number of Δ^1-pyrrolines and has been modified by Craig, Bulbrook and Hixon (*ibid.*, 1931, **53**, 1831).

Evidence regarding the presence of a carboxamido group in (A), formulated as (X), has been sought by treatment of the 4-acetamido derivative with thionyl chloride when, however, a vigorous reaction takes place with the formation of a dark resinous product. However, on treatment with phosphorus trichloride in toluene, the amide could be easily converted into the corresponding cyano compound (XI : R = Ph) in excellent yield. Cyano compounds are converted into amides with concentrated sulphuric acid or hydrochloric acid. In some cases, sulphuric acid reacts with cyano compounds in a complicated manner giving rise to mono- and disulphonic acids (Buckton and Hofmann, *Annalen*, 1856, **100**, 129). In fact, treatment of 4-acetamido derivative of (X : R = Ph) with concentrated sulphuric acid for 24 hours in the cold (5°-10°) has given rise to the

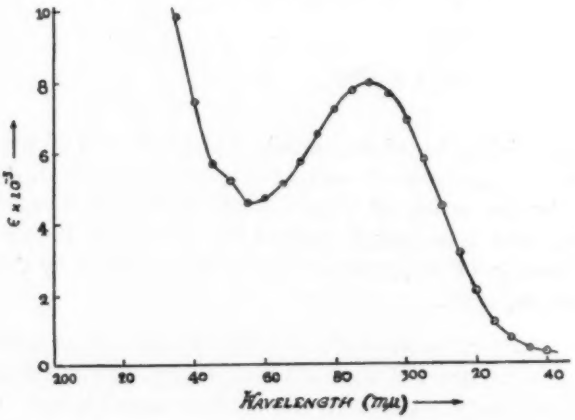
latter type of complex compound, namely, a sulphonic acid (m.p. above 300°) of undetermined constitution, which is readily soluble in cold water and is precipitated as the sodium salt (m. p. above 320°) with sodium acetate. Treatment of (X : R = Ph) with boiling hydrochloric acid gave rise to a dark, resinous product which proved extremely difficult to purify.

One of the general characteristics of cyano compounds is the tendency to polymerise under the influence of certain specific reagents. Malonitrile polymerises in the presence of sodium ethoxide to furnish trimer (Schenk and Finker, *Annalen*, 1928, **462**, 273). When the compound (XI : R = Ph), containing as it does two cyano groups attached to the same carbon atom as in the case of malonitrile, is treated with sodium ethoxide, a polymer in the form of a colorless, crystalline solid of high melting point (338-40°) has been obtained (vide Experimental). When all the above observations are taken into consideration, there is no doubt that the compound (A) could be best formulated as (X).

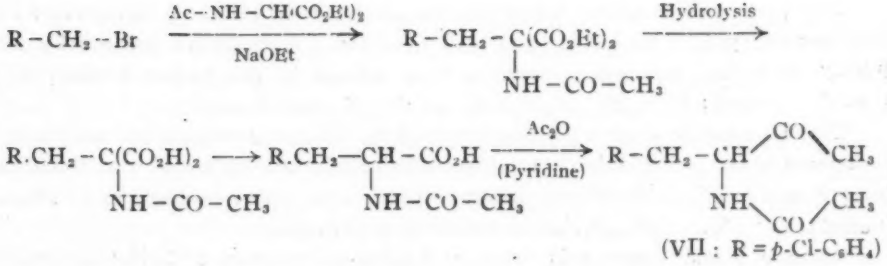
Ultraviolet absorption spectrum of the compound (X : R = Ph) was determined in ethanolic solutions with the help of a Beckman spectrophotometer using matched silica cells. The meter was calibrated against mercury lines and the light source was a hydrogen lamp. The molecular extinction values were plotted against the wave-length (Fig. 1). The curve shows a maximum at 290 mμ (ϵ = 7982.1) and a minimum at 255 mμ (ϵ = 4607.1). A slight break in the curve is observed in the range 245 mμ to 255 mμ.

FIG. 1

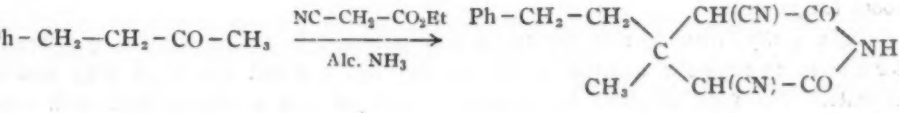
U. V. absorption spectrum of comp. X (R = Ph).



In connection with the above investigation, (α-acetamido-β-*p*-nitrophenyl)-ethylmethyl ketone (VII : R = *p*-NO_2-C_6H_4) has been prepared according to the method of Ghosh and Dutta (this *Journal*, 1955, **32**, 17). Starting from *p*-chlorobenzyl bromide, obtained by bromination of *p*-chlorotoluene in presence of benzoyl peroxide, (α-acetamido-β-*p*-chlorophenyl)-ethylmethyl ketone (VII, R = *p*-Cl-C_6H_4) has now been prepared according to the following scheme :



McElvain and Lyle (*J. Amer. Chem. Soc.*, 1950, **72**, 384) have demonstrated that 1-methyl-4-piperidone reacts with ethyl cyanoacetate in presence of ammonia to furnish the corresponding Guareschi imide. This shows that if the nitrogen atom is in the γ-position with respect to the keto group, the usual glutarimide is formed. It is therefore significant to observe that the reaction takes a different course if the nitrogen atom is in the α-position with respect to the keto group. The distinct influence of the α-nitrogen atom on the course of the reaction is further borne out by the observation, now made, that when β-phenylethylmethyl ketone itself is caused to react with ethyl cyanoacetate in presence of ammonia, the reaction takes the usual course and the expected glutarimide derivative (XII) is isolated.



(XII)

Work is in progress on the further study of the above reaction with various other α-acetamidoketones and will form the subject matter of a future communication.

EXPERIMENTAL

2 : 4-*Dimethyl*-3-*cyano*-3-*carboxamido*-4-*amino*-5-*benzyl*-Δ^1-*pyrroline* (X : R = Ph).—To anhydrous ethanol (55 c.c.), saturated at 0° with dry ammonia gas, (α-acetamido-β-phenyl)-ethylmethyl ketone (Cleland and Niemann, *J. Amer. Chem. Soc.*, 1949, **71**, 841) (10 g.) and ethyl cyanoacetate (12 g.) were added and the mixture was kept in the refrigerator in a well closed bottle for 96 hours. Removal of ethanol left a heavy liquid which, on cooling and standing, solidified to a crystalline mass. It was purified by dissolving in cold dilute HCl and precipitating by cold NH_4OH and finally crystallised from aqueous ethanol (charcoal) in colorless needles, m.p. 139-40°, which slowly turned brown on standing in the air. The compound was dried *in vacuo* at 90°-95° over P_2O_5. (Found : C, 66.8 ; H, 6.95 ; N, 21.07. $C_{15}H_{18}ON_4$ requires C, 66.66 ; H, 6.66; N, 20.74 per cent). It is insoluble in cold dilute alkali. The same compound (X : R = Ph) was obtained when cyanoacetamide was used in place of ethyl cyanoacetate.

The *picrate* was obtained in ethanolic solution as fine yellow needles, m.p. 178-80°. (Found : N, 19.42. $C_{15}H_{18}ON_4 . C_6H_3O_7N_3$ requires N, 19.64 per cent).

The *4-benzylidene-amino* derivative was obtained by refluxing (X : R = Ph ; 2 g.) with benzaldehyde (1 c.c.) in ethanol (40 c.c.) for 1 hour, when the Schiff's base quickly separated and was crystallised from ethanol in fine yellow needles, m. p. 210-11°. (Found : N, 15.58. $C_{22}H_{22}ON_4$ requires N, 15.64 per cent).

The *4-acetamido* derivative was obtained by treatment with acetic anhydride in presence of water, purified by trituration with cold dilute HCl. It was crystallised from glacial acetic acid-ethanol mixture (1 : 1) in brownish needles, m.p. 261-62°. (Found : N, 17.62. $C_{17}H_{20}O_2N_4$ requires N, 17.94 per cent).

When a glacial acetic acid solution of the above 4-acetamido derivative was saturated with dry HCl gas and then diluted with anhydrous ether, a colorless microcrystalline powder was precipitated, which was filtered, triturated five times with anhydrous ether and then kept overnight in a partially evacuated desiccator over alkali. The solid was found to have a pungent odour due to gradual liberation of HCl gas, and although it was found to be insoluble in water and melt at the same temperature as the parent 4-acetamido compound, it melted with decomposition and evolution of a gas, presumably HCl gas. It evolves CO_2 when treated with aqueous sodium bicarbonate, and its solution in cold concentrated nitric acid forms a precipitate of silver chloride, the percentage of which goes on decreasing with time during which the compound is allowed to stay. The above observations show that the 4-acetamido derivative yields an unstable hydrochloride, which gradually loses HCl at room temperature.

The *4-allylthiocarbamide* derivative was obtained in the usual way by refluxing for 6 hours an ethanolic solution of (X : R = Ph) and a slight excess of allyl *iso*thiocyanate. The solid obtained by removal of ethanol was triturated first with ether and then with cold dilute HCl and was finally crystallised from ethanol in colorless needles, m.p. 161-62°. (Found : N, 18.62 ; S, 8.41. $C_{19}H_{23}ON_5S$ requires N, 18.97 ; S, 8.67 per cent).

2 : 4-*Dimethyl-3-cyano-3-carboxamido-4-amino-5-p-nitrobenzyl-*Δ^1*-pyrroline* (X : R = *p*-NO_2-C_6H_4).—The method of procedure was the same as in the case of the previous compound (X : R = Ph). When the mixture was kept in the refrigerator for 96 hours, a red crystalline solid was obtained which was found identical with that obtained by removal of ethanol from the clear filtrate. The two solids were mixed together, and after purification by HCl-NH_4OH treatment, the compound was crystallised from ethanol, in which it was found to be sparingly soluble, in fine red needles, m.p. 213-14° (decomp.). (Found : C, 56.95 ; H, 5.38 ; N, 22.48. $C_{15}H_{17}O_3N_5$ requires C, 57.14 ; H, 5.39 ; N, 22.22 per cent .

The *picrate* was crystallised from ethanol in yellow needles, m p. 187-88°. (Found : N, 20 21. $C_{15}H_{17}O_3N_5 . C_6H_3O_7N_3$ requires N, 20.58 per cent).

The *4-acetamido* derivative was crystallised from glacial acetic acid in yellowish needles, m.p. 253-54°. (Found : N, 19.82. $C_{17}H_{19}O_4N_5$ requires N, 19.61 per cent).

The *4-allylthiocarbamide* derivative was prepared as in the previous case and was crystallised from ethanol, in which it was sparingly soluble, in yellowish rectangular plates which did not melt even at 300°. (Found : S, 7.58. $C_{19}H_{23}O_3N_6S$ requires S, 7.73 per cent).

Preparation of p-*Chlorobenzyl Bromide.*—Benzoyl peroxide (0.2 g.) (Kharasch *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 1405, used ascaridole for this preparation, without however, recording any experimental details) was added to a solution of *p*-chlorotoluene (35 g.) in CCl_4 (anhydrous, 35 c.c.) and to this mixture, heated on a water-bath at 79-80°, a solution of bromine (55 g.) in CCl_4 (anhydrous, 35 c.c.) was added dropwise during 3 hours. Heating was continued for 7 hours more and at the end the mixture was refluxed. After cooling, the mixture was treated with cold water and the CCl_4 layer separated, washed thoroughly with cold water and dried over anhydrous sodium sulphate. Removal of CCl_4 under reduced pressure left a mass which on scratching turned to a colorless crystalline solid (48 g.), m.p. 51° (lit. m.p. 51°).

Ethyl α-*Carbethoxy*-α-*acetamido*-β-p-*chlorophenylpropionate.*—Ethyl acetamidomalonate (60 g., prepared according to the method recorded by Ghosh and Dutta, *loc. cit.*) was added to a cooled solution of sodium (6.4 g.) in anhydrous ethanol (150 c.c.) and the mixture shaken thoroughly when the ester went into solution. After addition of *p*-chlorobenzyl bromide (55 g.), the mixture was heated under reflux on the water-bath for about 12 hours and cooled in ice, when the whole mass solidified. After filtration and washing thoroughly with cold water, the solid (70 g.) was crystallised from ethanol in fine colorless needles, m.p. 143-44°. (Found: N, 3.87. $C_{16}H_{20}O_5NCl$ requires N, 4.09 per cent).

α-*Carboxy*-α *acetamido*-β-p-*chlorophenylpropionic Acid.*—The above ester (70 g.) was treated with aqueous caustic soda solution (10%, 340 c.c.) and the mixture heated on the water-bath for about 4 hours, when the solid went into solution. The brownish solution was treated with Nuchar, filtered and acidified, under cooling, to Congo red with HCl (conc.). The precipitated solid (45 g.) was crystallised from aqueous ethanol in colorless rectangular plates, m.p. 113-15° (decomp.). (Found: N, 4.72. $C_{12}H_{12}O_5NCl$ requires N, 4.90 per cent).

That during the above hydrolysis the acetyl group has not been split off is supported by the observation of Snyder and Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 350) and of Ghosh and Dutta (*loc. cit.*). Moreover, the above compound is insoluble in dilute HCl and does not respond to any test for free amino group.

α-*Acetamido* β-p-*chlorophenylpropionic Acid.*—A mixture of the above dicarboxylic acid (40 g.) and water (150 c.c.) was heated under reflux on the wiregauge for about 3 hours, when CO_2 was evolved. The mixture was cooled and the solid filtered and crystallised from water in colorless rectangular plates (24 g.), m.p. 184°. (Found: N, 5.56; chem. equiv., 240.5. $C_{11}H_{12}O_3NCl$ requires N, 5.79 per cent. Chem. equiv., 241.5).

(α-*Acetamido*-β-p-*chlorophenyl*)-*ethylmethyl Ketone.*—A mixture of α acetamido-β-*p*-chlorophenylpropionic acid (25 g.), acetic anhydride (96 c.c.) and pyridine (75 c.c.) was heated under reflux on a water-bath for 5 hours (cf. Dakin and West reaction, *J. Biol. Chem.*, 1928, **78**, 91, 745, 757). Pyridine and excess of acetic anhydride were removed by steam-distillation and the mixture cooled in ice. The separated solid was filtered, triturated with 5% aqueous sodium bicarbonate solution and then finally crystallised from

aqueous ethanol in fine, colorless needles (14 g.), m. p. 119 20°. (Found: N, 5.52. $C_{12}H_{14}O_2NCl$ requires N, 5.84 per cent).

The 2:4-*dinitrophenylhydrazone* was crystallised from ethanol in yellow needles, m.p. 237-38°. (Found: N, 16.38. $C_{18}H_{18}O_5N_5Cl$ requires N, 16.68 per cent).

2:4-*Dimethyl*-3-*cyano*-3 *carboxamido*-4-*amino*-5-p-*chlorobenzyl*-Δ^1-*pyrroline* (X: R = *p*-Cl-C_6H_4).—Using (α-acetamido-β-*p*-chlorophenyl)-ethylmethyl ketone and proceeding as in the case of (X: R = Ph), (X: R = *p*-Cl-C_6H_4) was obtained and crystallised from ethanol in fine colorless needles, m.p. 191-92°. (Found: C, 58.86; H, 5.52; N, 18.21. $C_{15}H_{17}ON_4Cl$ requires C, 59.11; H, 5.58; N, 18.39 per cent). It is readily soluble in cold dilute HCl and insoluble in alkali.

The *picrate* was crystallised from ethanol in yellow needles, m.p. 181-82°. (Found: N, 18.12. $C_{15}H_{17}ON_4Cl$. $C_6H_3O_7N_3$ requires N, 18.37 per cent).

The 4-*acetamido* derivative, after trituration with cold dilute HCl, was crystallised from acetic acid-ethanol mixture (1:1) in fine colorless needles, m.p. 252°. (Found: N, 15.85. $C_{17}H_{19}O_2N_4Cl$ requires N, 16.16 per cent).

The 4-*allylthiocarbamide* derivative was crystallised from ethanol in colorless plates, m.p. 174°. (Found: N, 17.15; S, 7.52. $C_{19}H_{22}ON_5ClS$ requires N, 17.34; S, 7.93 per cent).

2:4-*Dimethyl*-3:3-*dicyano*-4-*acetamido*-5-*benzyl*-Δ^1-*pyrroline* (XI: R = Ph).—To a mixture of the 4-acetamido derivative (6 g.) of (X: R = Ph) and anhydrous toluene, kept in a flask protected from moisture, PCl_3 (1 g.) in anhydrous toluene (10 c.c.) was added dropwise under brisk stirring. The mixture was afterwards heated under reflux in an oil-bath at 130°-135° for 3 hours under stirring, when the solid went into solution. The solid (4.8 g.), which was deposited overnight, was filtered, thoroughly triturated with water and crystallised from ethanol in colorless needles, m.p. 202-203°. (Found: N, 19.16. $C_{17}H_{18}ON_4$ requires N, 19.04 per cent). It is insoluble in cold dilute alkali and in dilute HCl and does not contain any chlorine or phosphorus.

Treatment of (XI: R = Ph) *with Sodium Ethoxide: Formation of a Polymer.*—Sodium (0.8 g.) was dissolved in anhydrous ethanol (40 c.c.) and after the evolution of hydrogen had ceased, (XI: R = Ph; 2 g.) was added and the solution was heated under reflux for 8 hours in a flask protected from moisture. During this period the solution turned dark. After removal of the ethanol (25 c.c.) under reduced pressure, the mass was triturated with cold water when some quantity of a dark resinous mass was precipitated. The mixture was treated with charcoal and filtered, the alkaline solution yielding on acidification with acetic acid a solid which was thrice crystallised from ethanol in colorless plates, m.p. 338-40°. [Found: C, 69.15; H, 5.83; N, 18.94. $(C_{17}H_{18}ON_4)_n$ requires C, 69.38; H, 6.12; N, 19.04 per cent]. It is insoluble in cold dilute alkali and in dilute HCl.

α:α'-*Dicyano*-β-*methyl*-β-(2-*phenyl*)*ethylglutarimide* (XII).— To anhydrous ethanol (140 c.c.), saturated at 0° with dry ammonia gas, β-phenylethylmethyl ketone (30 g.) and ethyl cyanoacetate (46 g.) were added and the mixture was stored in the refrigerator in a well-closed bottle for 96 hours. During this period the container

was filled up with a crystalline solid, which was filtered and washed thoroughly with ethanol. The solid (ammonium salt of the imide) was dissolved in cold water and the clear aqueous solution acidified with cold dilute HCl. The precipitated solid was crystallised from ethanol in colorless needles, m.p. 224°. (Found: C, 68.12; H, 5.21; N, 15.24. $C_{16}H_{15}O_2N_3$ requires C, 63.32; H, 5.33; N, 14.94 per cent). It is readily soluble in cold dilute alkali and insoluble in dilute HCl.

The authors record their appreciation of the keen interest taken in this investigation by Dr. U. P. Basu, Director of the Institute. The absorption spectrum was measured by Mr. R. Bhattacharya of this Institute.

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DECOMPOSITION OF POTASSIUM PERSULPHATE IN PRESENCE OF *d*-MANNITOL

By Trilok Chand Jain

Kinetics of thermal decomposition of potassium persulphate solution in 0.14 *M* perchloric acid medium and in the presence of *d*-mannitol at 69.8° ± 0.1° is of the first order although its value is slightly less than that observed without this addendum.

Kolthoff and Miller (*J. Amer. Chem. Soc.*, 1951, **73**, 3055) studied the decomposition of potassium persulphate in acid medium and found the reaction to be of first order in 0.1 *M* perchloric acid at various temperatures. The persulphate decomposition proceeds according to the following mechanism :

(A) *Uncatalysed reaction* :

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^- \quad \ldots (1)$$

$$2\,SO_4^- + 2\,H_2O \longrightarrow 2\,HSO_4^- + 2\,OH \quad \ldots (2)$$

$$2\,OH \longrightarrow H_2O + \tfrac{1}{2}\,O_2 \quad \ldots (3)$$

(B) *Catalysed by hydrogen ion* :

$$S_2O_8^{2-} + H^+ \longrightarrow HS_2O_8^- \longrightarrow SO_4 + HSO_4^- \quad \ldots (4)$$

$$SO_4 \longrightarrow SO_3 + \tfrac{1}{2}\,O_2 \quad \ldots (5)$$

It is stated that (*a*) catalysed and uncatalysed reactions are independent reactions which occur simultaneously in persulphate solutions and that (*b*) reactions (1) and (4) are rate-determining.

Organic compounds, when oxidised by persulphate, furnish products from the nature of which it can be inferred that, in the first instance, the C--H link of the organic compound is attacked by persulphate or radicals from persulphate.

The resulting organic free radical then initiates a chain which involves the persulphate ion, and the overall reaction rate is found to be increased. For instance, Bartlett and Cotman (*ibid.*, 1949, **71**, 1419) found that saturated, buffered aqueous solution of persulphate with 1*M* methanol increased the rate of decomposition twenty-five fold, so also the oxidation of ethanol by the induced oxidation by persulphate (Kolthoff *et al.*, *ibid.*, 1951, **73**, 1733). In each case, the first step of decomposition of persulphate proposed is reaction (1), and the presence of organic compounds is, in general, found to increase the rate of decomposition.

The decomposition of persulphate in 0.14 *M* perchloric acid at 69.8° ± 0.1° has been investigated with and without added *d*-mannitol, and the rate has been observed to be of the first order. This first order rate constant in aqueous persulphate solution is of the

order of 6.81×10^{-3} (moles/litre, min^{-1}), while the first order rate constant in presence of *d*-mannitol is slightly lower (5.98×10^{-3} min^{-1}) and may be due to slightly increased frequency of the recombination of sulphate ion radicals in the solvation cage. That *d*-mannitol is attacked by the radicals from persulphate has been illustrated by examining the resulting solution, which shows the presence of *d*-mannose and turns slightly yellow. It is suggested that in this case the chain mechanism is not obtained as the subsequent reaction of the organic free radicals or the resulting compound from *d*-mannitol does not further attack persulphate ion. On the other hand, the products themselves are attacked with the consequent formation of the yellow solution. Recently Phillips (*Nature*, 1954, **173**, 1044) has observed that the action of ionising radiations on *d*-mannitol results in the formation of *d*-mannose and hydrogen peroxide, yield of which increases in presence of O_2, the ratio being two of hydrogen peroxide to one of *d*-mannose. In the present experiments also, slight formation of hydrogen peroxide has been observed. The previous workers did not obtain hydrogen peroxide as one of the products in persulphate decomposition. Its presence, in not too large quantities as well as of *d*-mannose in our experiments, seems to indicate that oxidation of *d*-mannitol by ionising radiations and by persulphate proceed by a similar mechanism.

EXPERIMENTAL

The values of first order rate constant, k_o, for three runs on the decomposition of persulphate without added *d*-mannitol are shown in Table I. The initial persulphate concentrations in these runs were 0.0113, 0.0502 and 0.0213 moles per litre. The agreement of all these runs as well as the linearity of the plot log c/c_o against time over 65% decomposition, confirms the first order character of the decomposition.

TABLE I

Rate constant for decomposition of $K_2S_2O_8$ *at* $69.8° \pm 0.1°$ *in* 0.14 *M*-$HClO_4$.

Conc. of persulphate c_o (mole/litre).	k (mole/litre, min^{-1}).	Mean k_o.
0.0113	7.16×10^{-3}.	
0.0213	6.53	6.81×10^{-3}
0.0502	6.74	

The value of k_o, 6.81×10^{-3} (mole/litre, min^{-1}), compares favourably with the reported value of 6.4×10^{-3} (m/l, min^{-1}) (Kolthoff and Miller, *loc. cit.*) at 70°

The quantitative effect of addition of varying concentration of *d*-mannitol was observed by making a similar log plot of the data. The results are reproduced in Table II, while the effect of changing persulphate concentration in presence of 0.11*M* *d*-mannitol is shown in Table III. Solutions stronger than 0.11 *M* in *d*-mannitol could not be conveniently investigated due to its limited solubility at room temperature.

TABLE II

Effect of d-*mannitol concentration on the decomposition of* $K_2S_2O_8$.

$K_2S_2O_8$ conc. (m/l)	0.0395	.0406	0.0399	0.0426	0.0426	0 0399	0.0411
d-Mannitol (m/l)	0.045	0.011	0.0011	0.00275	0.0055	0.00055	0.00011
k (m/l, min^{-1}) $\times 10^3$	6.12	5.91	5.96	6.20	5.96	5.93	5.82

Mean $k = 5.98 \times 10^{-3}$ (mole/litre, min^{-1})

TABLE III

Rate constant for different conc. of persulphate in presence of 0.11 *M* d-*mannitol.*

$HClO_4 = 0.14$ *M*. Temp $= 69.8 \pm 0.1°$.

$K_2S_2O_8$ conc. (mole/litre)	0.77	0.0205	0.00936
k (mole/litre, min^{-1}) $\times 10^3$	5.93	5.82	6.13

Mean $k = 5.96 \times 10^{-3}$

The first order rate constants are not dependent on either persulphate concentrations or on the concentrations of *d*-mannitol. However, the value of k is slightly less than the value of k_0.

Analyses.—Persulphate solutions were estimated iodimetrically. To 10 c.c. of persulphate solution were added 1 g. of KI and 10 c.c. of $6N$-H_2SO_4, and the mixture was allowed to stand for 30 minutes in dark in glass-stoppered bottles. The liberated iodine was titrated against standard thiosulphate solution. *d*-Mannitol or *d*-mannose was found not to interfere with the estimation. The amount of H_2O_2 formed during the 70% decomposition is of the order of 10^{-4} mole/litre and does not substantially contribute to the liberation of iodine. The solutions of persulphate and *d*-mannitol were preheated and then mixed and immediately a sample was drawn out to obtain the initial concentration of persulphate. Sample solutions were also tested qualitatively for hydrogen peroxide and *d*-mannose by the usual analytical methods, namely, tests for hydrogen peroxide were made with titanium sulphate and vanadic acid, and for *d*-mannose, Molisch test was applied. No attempt was, however, made to estimate the reaction products quantitatively.

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ANALYTICAL STUDIES OF PHOTOCHEMICALLY DEGRADED JUTE. PART I

By W. G. Macmillan and H. P. Bhattacherjee

In the progressive photochemical degradation of jute, the nature and the rate of chemical changes of the carbohydrate fractions have been studied. Yield of holocellulose and of α-cellulose decreases with time of exposure with a progressive rise in fluidity of the α-cellulose in cuprammonium solution. Copper number of jute rises after exposure to light, but no increase is recorded in the isolated carbohydrate fraction.

The photochemical degradation of cotton and other cellulosic materials has been studied by various workers under different conditions, and the results of the various observations lead to the general conclusion that the action of light results in the formation of oxycelluloses (Heuser, *Cellulose Chem.*, 1944, 481). In addition to loss in tensile strength, the changes which are observed are, increase in cuprammonium fluidity, copper number and silver number with little change in methylene blue absorption. Rise in fluidity is roughly correlated with the loss in tensile strength and is often regarded as an index of the extent of photochemical degradation of cotton (Egerton, *J. Soc. Dyers & Col.*, 1947, **63**, 161). In jute, however, a comprehensive analytical study has not yet been carried out although various workers have studied the subject in various aspects from time to time. Turner (*ibid.*, 1920, **36**, 165) has observed that jute undergoes photochemical degradation more rapidly than other vegetable fibres, and this has been supported by Bot and Vreeswijk (*Melliand Textilber.*, 1939, **20**, 115). Macmillan and Basu (*J. Text. Inst.*, 1947, **38**, T350) have reported three additional effects, viz., extreme dissolution in alkali, decrease in lignin content and lintering, especially in water. Callow and Speakman (*J. Soc. Dyers & Col.*, 1949, **65**, 758) have shown that all the main components of jute undergo degradation by light as indicated by the reduction in the values of Norman and Jenkins cellulose, the lignin and the xylan contents of the exposed materials. They have also noted that water-soluble reducing and acidic bodies are formed during irradiation and concluded that the reducing substances are derived from cellulose chain-fission while acidic bodies are developed from the degradations of component other than cellulose. In addition, they have observed that demethylation takes place in lignin and have expressed the view that the degradation of lignin leads to the formation of *o*-diphenols and, ultimately, *o* quinones which contribute to the yellowing of jute.

Detailed information regarding the nature and extent of the chemical degradation of the different constituents of jute with progressive photochemical reaction, however, is lacking. The present investigation is designed therefore to gather some preliminary knowledge about these chemical changes in the different constituents which would be of assistance in understanding their relationship with the strength loss as well as in elucidating the mechanism of the photochemical degradation, which is much enhanced in jute. The changes observed in the carbohydrate fractions are mainly described in this paper.

EXPERIMENTAL

A good quality of tossa jute, taken from the middle portions of strands, was de-oiled by alcohol-benzene mixture, washed with distilled water and used in the experiments after air-drying.

Exposure to Light.—A carbon arc fadeometer of FDA-R (Atlas Electric Devices Co.) type with wet wicks was used for light exposure. The jute strands, well combed, were cut into a length of 7 inches and suitably mounted on the specimen holders, 2 g. of jute being uniformly spread over each holder covering a space of about 7″ × 2.5″, which was the available space on each holder. To facilitate uniformity of photochemical reaction, the samples were teased by hand after every 5 hours of exposure. Twenty samples were thus prepared and exposed simultaneously, a set of five being withdrawn after a regular interval of 25 hours for analysis. Throughout the whole experiment the exhaust air of the fadeometer recorded a temperature of 37°-40° and a relative humidity of about 50%.

Chemical Analysis

The exposed samples, collected from five specimen holders, were cut into small lengths, well mixed and subjected to analysis by the following procedures, the results being expressed on oven-dry basis.

Water solubility.—The sample (1.0 g.) was refluxed with distilled water (50 c.c.) for 30 minutes, filtered through a sintered glass crucible, the filtrate being collected and the fibre washed with 200 c.c. of distilled water before drying. The p_H of the filtrate was measured with a Hellige comparator.

Acetyl content was determined by estimating the steam-volatile acids, liberated by a previous alkaline hydrolysis (Bhattacherjee and Callow, *J. Text. Inst.*, 1952, **43**, T56).

Alkali solubility.—The sample (0.5 g.) was refluxed for 1 hour with 1% NaOH solution, with a liquor ratio of 100 : 1, filtered and followed by a dilute acid (N/10-HCl) treatment.

Holocellulose.—Two successive treatments, each with a 0.7% sodium chlorite solution for 2 hours in a boiling water-bath at p_H 4, with liquor ratio 50 : 1 were given.

α-Cellulose.—The A.C.S. method (Ritter, *Ind. Eng. Chem., Anal. Ed.*, 1929 **1**, 52) was adopted and α-cellulose was prepared from the holocelluloses.

Degree of Polymerisation.—Fluidity of α-cellulose in cuprammonium solution was determined in presence of cuprous chloride (Launer and Wilson, *Anal. Chem.*, 1950, **22**, 455) and the D.P. values calculated from the fluidity figures.

Copper Number.—A procedure similar to that of the modified Schwalbe-Braidy method (Dorée, "The Methods of Cellulose Chemistry", 1947, p. 34) was followed using 0.25 g. of the sample and 50 c.c. of alkaline copper solution.

Acid Value.—The iodimetric method using iodide-iodate mixture was followed on cation-free samples (Sarkar, Chatterjee and Mazumdar, *J. Text. Inst.*, 1947, **38**, T323).

DISCUSSION

As previously noted (Callow and Speakman, *loc.cit.*), the solubility of jute in water increases with progressive photochemical reaction (Table I) with a gradual decrease in the p_H of the aqueous extract, indicating the formation of acidic bodies. The development of acidity has been explained to be due to the probable degradation of the polyuronide hemicelluloses and lignin.

TABLE I

Effect of light on water solubility, alkali solubility and acetyl content of jute.

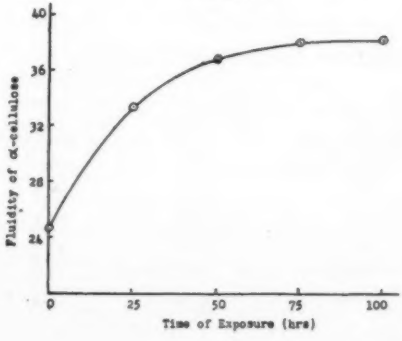
Time of exposure.	Water solubility.	p_H of aqueous extract.	Acetyl content of water-extracted sample*	Alkali solubility.
1. Nil	0.70%	6.2	3.22%	11.2%
2. 25 hrs	2.4	4.5	3.21	22.4
3. 50	4.9	4.1	2.99	28.4
4. 75	6.1	4.0	2.79	36.7
5. 100	7.7	3.9	2.76	37.0

* Expressed on untreated exposed samples.

The acetyl content of the water-extracted samples is found to be diminished with time of exposure, indicating that the acetyl groups are either split off liberating acetic acid which is extracted with water, or are lost with the water-soluble degradation products with which they are combined. Splitting of acetyl groups with the formation of acetic acid in irradiation of acetylated jute has been reported (Callow and Speakman, *loc. cit.*) and in the case of jute, acetic acid thus liberated might be an additional contributory factor to the increased acidity of the aqueous extract. A detailed study on the mode of formation of water-soluble substances having reducing and acidic properties, by irradiation of jute, will be communicated later. Increased alkali-solubility undoubtedly accounts for the photochemical degradation of all the major components of jute. It is also possible that the dissolution of the carbohydrate fractions is further facilitated due to the oxidation of lignin, which is more easily affected than the other components.

Table II shows that the yield of holocellulose decreases progressively with exposure to light. The α-cellulose content of holocellulose first shows a slight increase which is followed by a gradual decrease. When expressed on jute, values of the α-cellulose content show a gradual decrease all through, the magnitude of decrease being small in the initial stages of exposure. The apparent increase in the α-cellulose content of the holocelluloses probably accounts for the preferential dissolution of some amount of degraded hemicelluloses during their isolation in the respective samples. The rate of degradation of the α-cellulose is indicated by the rise in cuprammonium fluidity,

FIG. 1



illustrated in Fig. 1 and the corresponding decrease in the D.P. values as calculated and shown in Table II. The trend of the rise in fluidity of the α-cellulose appears to be similar to that observed in cotton, the rate of change being gradually decreased with time of exposure (Egerton, *loc. cit.*).

TABLE II

Effect of light on the yield of holocellulose and α-cellulose and the degree of polymerisation of α-cellulose of jute.

Time of exposure.	Holocellulose.	α-Cellullose (on holocellulose).	α-Cellulose (on jute).	D P. of α-cellulose.
1. Nil	84 9%	74.0%	62.8%	840
2. 25 hrs.	83.1	74.9	62.2	630
3. 50	81.0	74.6	60.4	560
4. 75	78.9	71.4	56 4	540
5. 100	75.7	70.0	53.0	530

Although the copper number of jute rises rapidly with time of exposure, as shown in Table III, that of the isolated holocelluloses does not show any increase ; on the contrary, it is slightly decreased with prolonged exposure, indicating that the reducing substances contributing to the copper number of jute are formed mainly from lignin. Because demethylation takes place in the lignin molecule leading to the probable formation of polyhydroxy benzene derivatives, it is likely that these lignin degradation products would contribute substantially to the increased copper number of exposed jute. It is also possible that the reducing substances are produced from the carbohydrate fractions but are subsequently eliminated during their isolation. It appears that the total reducing groups in the holocellulose fraction do not increase even though the carbohydrate chains, both of hemicelluloses as well as of cellulose, have undergone considerable degradation. The possibility of conversion of the aldehydic groups to carboxyl due to oxidation has also been examined without any positive indication, as shown by a gradual decrease in the acid values instead of any increase.

Table IV shows that even with 100 hours of exposure the acid value of the isolated α-cellulose remains unchanged. When, however, the figures are expressed on jute, a variation is observed which is due to the difference in the yield of α-cellulose of the samples (Table II).

TABLE III

Effect of light on the copper number of jute and the isolated holocelluloses.

Time of exposure.	Copper number			Acid value of holocellulose.*	Acid value of holocellulose expressed on jute.*
	Jute.	Holocellulose.	Holocell.expressed on jute.		
1. Nil	1.4	0 25	0.21	26.8	22.7
2. 25 hrs.	5 4	0.27	0.22	24.4	20.3
3. 50	7.4	0.19	0.15	24.1	19 5
4. 75	9.1	0.18	0.14	23.6	18.6
5. 100	10.4	0 18	0.14	21 4	16.2

* Milliequivalents per 100 g.

TABLE IV

Acid value of α-cellulose of jute before and after light exposure.

Time of exposure (in hour)	Nil	100
* Acid value of α-cellulose	0.65	0.65
* Acid value of α-cellulose expressed on jute	0.41	0.34

* Milliequivalents per 100 g.

Figs. 2 and 3 illustrate the nature of the relationship between the fluidity of α-cellulose and the alkali-solubility and copper number of light-exposed jute respectively. It will be observed that up to 50 hours of exposure, the rise in fluidity is practically proportional to the increase in alkali-solubility and copper number and, above 50 hours, the rate of change of fluidity is comparatively decreased.

FIG. 2

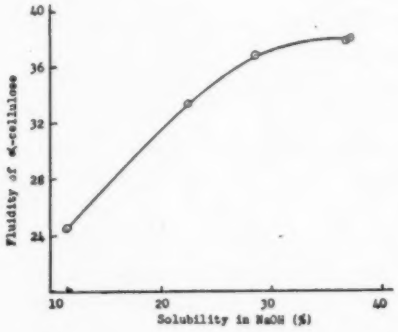
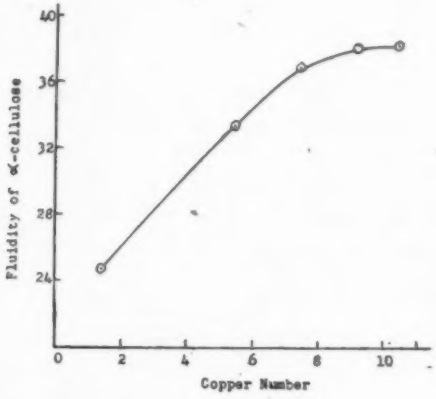


FIG. 3



CONCLUSIONS

1. In progressive photochemical degradation of jute, solubility in water and alkali increases with gradual decrease in acetyl content of the water-extracted samples.

2. The yield of holocellulose and of α-cellulose is progressively diminished with increased photochemical reaction.

3. Cuprammonium fluidity of α-cellulose of jute rises with time of exposure to light, the D.P. values being reduced from 840 of unexposed jute to 630 after 25 hours and to 530 after 100 hours of exposure.

4. Copper number of jute rises with exposure to light but no such rise is observed in the isolated holocellulose, indicating that lignin degradation products may be mainly responsible for the increase in copper number of light-exposed jute.

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POTASSIUM METAPERIODATE AS A VOLUMETRIC REAGENT. PART VI. BROMOMETRIC METHOD

By Ram Chand Paul and Apar Singh

Tartar emetic, Fe_3SO_4, KCN, $Na_2S_2O_3$, KCNS, H_2SO_3, $Na_2S_4O_6$ $SnCl_2$ and K_4FeCy_6 have been estimated with potassium metaperiodate in the presence of KBr and HCl using a bromometric method.

In previous communications (this *Journal*, 1952, **29**, 34, 517; 1953, **30**, 143; *Res. Bull. East Panjab Univ.*, 1952, **17**, 51) potassium metaperiodate has been developed as a volumetric reagent for the direct and indirect estimations of various inorganic cations and anions. The same reagent has been further developed as a bromometric reagent for the oxidation of various substances like potassium cyanide, potassium sulphocyanide, potassium ferrocyanide etc., which are either not easily oxidised or require pre-oxidation with iodine monochloride or hypoiodous acid. It has been found in the present investigation that the excess of potassium metaperiodate reacts with potassium bromide in the presence of hydrochloric acid according to the equation:

$$IO_4^- + 7Br^- + 8H^+ \longrightarrow IBr + 3Br_2 + 4H_2O$$

and the excess is titrated back with standard arsenious oxide solution according to the equation, developed by Lang (*Z. anorg. allgem. Chem.*, 1925, **144**, 75) for KIO_3:

$$IBr + 3Br_2 + As^{3+} + HCN \longrightarrow ICN + 7Br^- + 3As^{5+} + H^+.$$

At the end of the titration, the total periodate iodine appears as iodine cyanide and the completion of the reaction is shown by the disappearance of starch-blue colour (cf. Singh, this *Journal*, 1953, **30**, 143). Potassium metaperiodate reacts with various substances in accordance with the equations:

$$2IO_4^- + 3As_2O_3 + 2HCN + 2H^+ \longrightarrow 2ICN + 3As_2O_5 + 2H_2O$$

$$2IO_4^- + 3Sb_2O_3 + 2HCN + 2H^+ \longrightarrow 2ICN + 3Sb_2O_5 + 2H_2O$$

$$2IO_4^- + 3N_2H_4 + 2HCN + 2H^+ \longrightarrow 2ICN + 3N_2 + 8H_2O$$

$$4IO_4^- + 3S_2O_3^{2-} + 4HCN \longrightarrow 4ICN + 6SO_4^{2-} + 2H^+ + H_2O$$

$$IO_4^- + 3Sn^{2+} + HCN + 7H^+ \longrightarrow ICN + 3Sn^{4+} + 4H_2O$$

$$IO_4^- + 6Fe^{2+} + HCN + 7H^+ \longrightarrow ICN + 6Fe^{3+} + 4H_2O$$

$$IO_4^- + 3SO_3^{2-} + HCN + H^+ \longrightarrow ICN + 3SO_4^{2-} + H_2O$$

$$7IO_4^- + 3S_4O_6^{2-} + 7HCN + 2H_2O \longrightarrow 7ICN + 12SO_4^{2-} + 11H^+$$

$$IO_4^- + 4Br^- + 3HCN + 5H^+ \longrightarrow CNBr + IBr + 4H_2O$$

$$4IO_4^- + 7Br^- + 3CNS^- + 8H^+ \longrightarrow 3CNBr + 3SO_4^{2-} + 4IBr + 4H_2SO_4$$

$$IO_4^- + 6FeCy_6^{4-} + HCN + 7H^+ \longrightarrow ICN + 6FeCy_6^{3-} + 4H_2O$$

EXPERIMENTAL

The titrations here recorded were carried out in a flask similar to that used by Mayr and Peyfuss (*Z. anorg. allgem. Chem.*, 1915, **92**, 127). A known weight of the substance or its solution in water was taken in a conical flask and 30 to 40 c.c. of water, 1.0 g. of KBr and 20 c.c. of HCl (1 : 1) were added to it. A known excess of 0.1*N* potassium metaperiodate (30-40 c.c.) was added to the reaction mixture from the burette. The flask was corked and allowed to stand in cold water for 5 to 10 minutes till the oxidation was complete. The cork was opened and the reaction mixture titrated against standard arsenious oxide solution in the presence of starch solution. The arsenious oxide solution was added in portions of 0.5 to 1 c.c. until the solution was permanently dark brown. 0.5*N*- KCN (10 c.c.) was added and the solution allowed to stand till the blue colour appeared. The whole mixture was then titrated very slowly with constant shaking against standard 0.1*N* potassium metaperiodate till the disappearance of the blue colour. In the case of potassium ferrocyanide, the excess of bromine was immediately titrated against standard arsenious oxide solution, in order to prevent the bromination of the ferrocyanide ion.

Several titrations were performed in each case. From the volume of potassium metaperiodate used, the amount of each substance was calculated. The results of various titrations are recorded in the following table.

TABLE I

	Tartar emetic			Hydrazine sulphate			Ferrous sulphate	
0.1*N*-KIO_4.	Taken.	Found.	0.1*N*-KIO_4.	Taken.	Found.	0.1*N*-KIO_4.	Taken.	Found.
10.75 c.c.	0.1795 g.	0.1795 g	9.95 c.c.	0.0325 g.	0.0323 g.	10.10 c.c.	0.2780 g.	0.2807 g.
14.00	0.2334	0.2338	13.00	0.0418	0.0419	13.00	0.3614	0.3614
18.30	0.3052	0.3056	19.10	0.0618	0.0619	17.50	0.4826	0.4905
22.30	0.3760	0.3724	23.00	0.0747	0.0747	24.40	0.6631	0.6863
26.55	0.4438	0.4434	17.00	0.0553	0.0553			

1 c.c. of 0.1*N*-KIO_4 ≡ 0.0167 g. tartar emetic ≡ 0.00325 g. hydrazine sulphate ≡ 0.0278 g. $FeSO_4, 7H_2O$.

	Potassium cyanide			Sodium thiosulphate			Potassium sulphocyanide	
11.40 c.c.	0.0371 g.	0.0371 g.	10.10 c.c.	0.0310 g.	0.0313 g.	9.70 c.c.	0.01212 g.	0.01175 g.
14.90	0.0486	0.0484	13.00	0.0403	0.0403	12.80	0.01576	0.01552
21.60	0.0710	0.0702	17.00	0.0527	0.0527	19.00	0.02303	0.02303
26.40	0.0858	0.0858	19.00	0.0589	0.0589	20.00	0.02424	0.02424
			21.80	0.0682	0.0676	22.90	0.02788	0.02776

1 c.c. of 0.1*N*-KIO_4 ≡ 0.00325 g. KCN ≡ 0.003102 g. $Na_2S_2O_3, 5H_2O$ ≡ 0.001212 g. KCNS.

TABLE I (contd.)

	Sulphurous acid			Sodium tetrathionate			Stannous chloride	
0.1*N*-KIO_4.	Taken.	Found.	0.01N-KIO_4.	Taken.	Found	0.01N-KIO_4.	Taken.	Found.
12.30 c.c.	0.0500 g.	0 0504 g.	12.60 c.c.	0.0243 g.	0.0243 g.	9.60 c.c.	0.1083 g.	0.1013 g.
15 80	0.0650	0.0648	18.00	0 0347	0.0347	12.30	0.1401	0.1387
18.30	0.0750	0 0750	21.80	0.0417	0.0420	16 20	0.1841	0.1827
24.30	0.0954	0.1002	30.60	0 0590	0 0590	22 60	0.2599	0.2549
27 70	0.1125	0 1135	41.50	0.0799	0.0801			

1 c.c. of 0.1*N*-$KIO_4 \equiv 0.0041$ g. H_2SO_3. $\equiv 0.001929$ g. $Na_2S_4O_6$. $\equiv 0.1128$ g. $SnCl_2H_2O$.

Potassium ferrocyanide.

10.00	0.4230	0.4220
13.30	0.5499	0.5612
7.00	0.2935	0.2954
11.20	0.4653	0.4726

1 c.c. of 0.1*N*-$KIO_4 \equiv 0.0422$ g. $K_4Fe(CN)_6$

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EQUATION FOR THE TOTAL POTENTIAL OF CLAY MEMBRANE ELECTRODES

By B. Chatterjee

The derivation of the equation for the total potential of clay membrane electrodes is based on the membrane permeability theory, proposed simultaneously by Teorell (*Proc. Soc. Expt. Biol. Med.*, 1935, **33**, 282) and Myers and Sievers (*Helv. Chim. Acta*, 1936, **17**, 649, 665, 987), and on the Donnan distribution of ions. Let a_1 and a_2 be the activities of potassium chloride solutions on two sides of the membrane, which is saturated in this case with potassium ions, and let A be the charge on the membrane expressed as potassium ion activity. At equilibrium, two Donnan distributions are attained, one at each phase of the boundary, and there will also appear a liquid-junction inside the membrane, as shown in sketch A.

Sketch A

KCl	Donnan equilibrium	Liquid junction	Donnan equilibrium	KCl
(a_1)	I	Clay membrane	II	(a_2)
E_1		E_3		E_2

The total potential of the clay membrane electrode will therefore be an algebraic sum of E_1, E_2 and E_3.

Let us now consider the ionic distribution on the attainment of Donnan equilibrium, say, at the left hand phase in the sketch. Some KCl will enter inside of the membrane to establish the equilibrium. If y moles of KCl enter the membrane, then

$$(a_{1K^+} \times a_{1\,Cl^-}) = (A + y)\, y$$

(outside of membrane) (inside of membrane)

since A, the negative charge on the membrane, is equal to the balancing K^+ ions.

For a dilute KCl solution, $a_{K^+} = a_{Cl^-}$.

Therefore, $a_{1(KCl)}^2 = Ay + y^2$.

or
$$y = \frac{-A + \sqrt{A^2 + 4a_{1(KCl)}^2}}{2} = \tfrac{1}{2}A + \tfrac{1}{2}p_1,$$

where $p_1 = \sqrt{A^2 + 4a_{1(KCl)}^2}$.

Assuming that the composition of the bulk solution is not changed by the entrance of a small amount of KCl into the membrane, the compositions of the inside and outside solutions will be as follows, say, for compartment I (Sketch A).

Outside solution : $a_{K^+} = a_1$ (say) $= a_{Cl^-}$

Inside solution : $a_{K^+} = \tfrac{1}{2}(A + p_1)$

$a_{Cl^-} = -\tfrac{1}{2}(A - p_1)$.

Therefore, $E_2 = \frac{RT}{F} \ln \frac{a_1}{\frac{1}{2}(A+p_1)}$.

Similarly for the compartment II,

$$E_1 = -\frac{RT}{F} \ln \frac{a_2}{\frac{1}{2}(A+p_2)},$$

where a_2 denotes the activity of K^+ ions and p_2 corresponds to p_1 in compartment I.

The liquid-junction potential between the Solutions I and II within the membrane is given by the Henderson formula for 1 : 1 electrolyte.

$$E_3 = \frac{RT}{F} \frac{(v_1^+ - v_1^-) - (v_2^+ - v_2^-)}{(v_1^+ + v_1^-) + (v_2^+ + v_2^-)} \ln \frac{v_1^+ + v_1^-}{v_2^+ + v_2^-}$$

where $v_1^+ = \frac{1}{2}U_+ (A+p_1)$, $v_1^- = -\frac{1}{2}U_- (A-p_1)$,

$v_2^+ = \frac{1}{2}U_+ (A+p_2)$, $v_2^- = -\frac{1}{2}U_- (A-p_2)$

and U_+ and U_- are the mobilities of the K^+ and Cl^- ions respectively. Substituting these values in the above equation for E_3, we have,

$$E_3 = \frac{RT}{F} - \frac{U_+ - U_-}{U_+ + U_-} \ln \frac{U_+ - U_-}{U_+ - U_-} + \frac{p_1}{A} \Big/ \frac{U_+ - U_-}{U_+ + U_-} + \frac{p_2}{A}.$$

When A is large in comparison of a_1 and a_2, which is a prerequisite for a permselective membrane, the junction potential reduces to zero, since p_1/A and p_2/A are both equal to unity. Consequently, the total membrane potential, E, is given by

$$E = E_1 + E_2 = \frac{RT}{F} \ln \frac{a_1}{\frac{1}{2}(A+p_1)} \times \frac{\frac{1}{2}(A+p_2)}{a_2} = \frac{RT}{F} \ln \frac{a_1}{a_2}$$

since here also $p_1/A = p_2/A = 1$, when A is large.

The E.M.F. between solutions separated by a membrane for which A is large compared to the ionic activities to be measured, is thus given by the well known Nerest equation,

$$E = \frac{RT}{F} \ln \frac{a_1}{a_2}.$$

It has been found that the observed values of the potentials of clay membrane electrodes in solutions of ammonium, potassium, sodium, calcium, magnesium, barium, zinc, copper, cobalt and manganese salts, within specified ranges of activities, are in agreement with those calculated from this equation. It should, however, be mentioned that the above equation is valid only when the cations on both sides of the membrane are similar. With dissimilar cations, the equation for the total potential of the clay membrane electrodes becomes somewhat complicated. This can be worked out from a consideration of the Henderson equation and the 'mobility ratios' in the membrane of the cations concerned.

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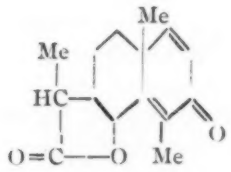
SESQUITERPENES AND RELATED SUBSTANCES. PART III*. SYNTHETIC STUDIES ON SANTONIN

By Phanindra Chandra Dutta and Nikhil Ranjan Ghosh

Experiments have been described leading to the synthesis of a dihydrosantonin. Although it could not be isolated in a crystalline state, the identity of the compound has been established through infra-red studies and chemical reactions.

Attempts at the synthesis of santonin or its stereoisomerides have been very scant till the last few years. The reasons may be ascribed to the building up of a dienone system extremely susceptible to rearrangement under acidic conditions and to the presence of a *trans*-γ-lactone ring fused in an angular way to a comparatively simple 9-methyldecalin molecule.

The structure of santonin has been established by Clemo, Haworth and Walton (*J. Chem. Soc.*, 1930, 1110, 2579) as below.



Paranjape, Phalnikar, Bhide and Nargund (*Rasayanam*, 1943, **1**, 233; *Proc. Ind. Acad. Sci.*, 1944, **A**, **19**, 381; *Nature*, 1944, **153**, 141) first announced the synthesis of the optically active santonin, identical with the natural one, without the use of any optically active reagent. The unusual features of this investigation have been criticised from different laboratories, and we believe no reply has yet been made by the authors.

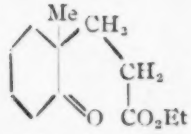
Experiments were initiated by one of us in 1947 to realise the synthesis of santonin or its stereoisomerides in collaboration with Banerjea. As it was not possible to continue the investigations under the then existing circumstances, a preliminary note was published, indicating the main line of synthesis (Banerjea, *Science & Culture*, 1948, **13**, 347; *Chem. Abs.*, 1948, **42**, 5890). The synthetic experiments, recently carried out successfully to the penultimate stage according to the original scheme adumbrated in the note communicated by Banerjea (*loc. cit.*), have led to the formation of a stereoisomer of dihydrosantonin, as indicated by its reactions and infra-red spectra (Dutta, *ibid.*, 1953, **19**, 164; cf. Dutta *et al.*, *Chem. & Ind.*, 1955, 170). In the meantime, several attempts towards the synthesis of santonin have been put on record (Clemo and McQuillin, *J. Chem. Soc.*, 1952, 3835, 3839; Gunstone and Heggie, *ibid.*, 1952, 1137, 1354; *J. Appl. Chem.*, 1954, **4**, 291). The Japanese workers (Abe *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 2567) have first announced the

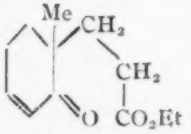
* The following publications constitute Part I and II respectively of this series:-(i) This *Journal*, 1940, **17**, 649 and (ii) this *Journal*, 1941, **18**, 233.

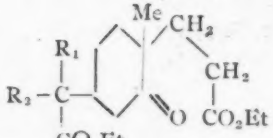
synthesis of two optically inactive stereoisomerides of santonin and then the total synthesis of α-santonin and β-santonin (*Proc. Japan Acad.*, 1954, **30**, 116).

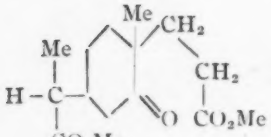
The main purpose of this investigation is to explore the various synthetic routes to build up the gross structure of the dihydrosantonin molecule. If the reactions proceed in the expected path, it is hoped to direct the synthesis in a more stereospecific way so that the disturbing factor of stereoisomerism may be minimised leading to the possibility of isolating crystalline products. This is all the more desirable because dihydrosantonin or santonin contains four asymmetric centres, some of which are not amenable to the usual inversion processes. Due to recent advances in the fundamental conception of stereospecific synthesis in alicyclic systems, it is now possible to assign definite stereochemical configurations to various reaction products in many cases, specially with the help of conformational analysis, developed by Barton and others.

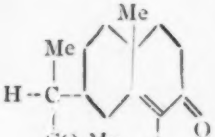
Returning to the actual problem of synthesis, it can be schematically represented below.

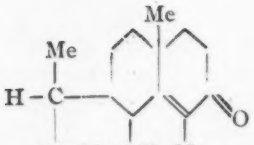

(I)

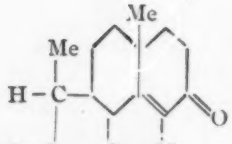

(II)

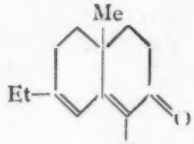

(III : R_1 = H, R_2 = CO_2Et)
(IV : R_1 = Me, R_2 = CO_2Et)

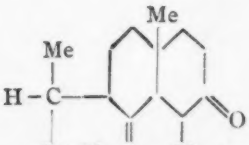

(V)


(VI)


(VII)


(VIII)

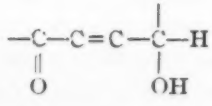

(IX)


(X)

o-Methyl*cyclo*hexanone has been condensed with ethyl β-bromopropionate in presence of sodamide in ethereal solution and the crude condensation product has been

purified through condensation with ethyl oxalate and subsequent hydrolysis with barium hydroxide (Dutta, this *Journal*, 1940, **17**, 649). The condensation product from acrylonitrile and *o*-methyl*cyclo*hexanone in presence of basic catalysts (Frank and Pierle, *J. Amer. Chem. Soc.*, 1951, **73**, 724) has been found to contain an appreciable amount of 1:6-isomer, as has been revealed in the subsequent stages of synthesis. The purified ester (I) has been brominated in dilute ethereal solution in the cold, but the bromo derivative could not be isolated in a pure condition and so it has been directly dehydrohalogenated by heating with quinoline (Dutta, *Sceince & Culture*, 1947, **13**, 258 ; this *Journal*, 1949, **26**, 109). As we required large quantities of the unsaturated ester (II), it was found advantageous to brominate the keto-ester without any solvent (Conrad and Kriechgauer, *Ber.*, 1897, **30**, 856) and to dehydrohalogenate it as before (cf. Mukherjee, this *Journal*, 1948, **25**, 161), because the saturated ester present to some extent in (II) should not interfere with the subsequent reactions The unsaturated keto-ester (II) is allowed to react with ethyl malonate in presence of a trace of sodium ethoxide in alcoholic solution in the cold, when the addition product (III) is isolated in a very good yield (Bartlett and Woods, *J. Amer. Chem. Soc.*, 1940, **67**, 2937). Methylation of the Michael addition product has been found to be a very delicate step (Mukherjee, *loc. cit.*) and in presence of a trace of sodium ethoxide, methylated product (IV) tends to undergo retrogression to a considerable extent with the regeneration of the unsaturated keto-ester (II). The latter can, however, be utilised for the Michael reaction again to afford (III) in a very good yield. By repeating the process, satisfactory yield of (IV) can be obtained. Experiments have also been successfully carried out to condense both the steps into one by using ethyl methylmalonate as an addendum in the Michael reaction with the unsaturated keto-ester (II) in presence of a trace of sodium ethoxide in the cold (Warner and Moe, *J. Amer. Chem. Soc.*, 1949, **71**, 2586 ; cf. Gunstone and Tulloch, *J. Appl. Chem.*, 1954, **4**, 291). The methylated ester (IV) has been hydrolysed by refluxing with acetic acid and hydrochloric acid for a prolonged period and the keto-ester (V) has been isolated in a very good yield on esterification. The percentage of carbon in the analytical result was always found to be rather low in the ester (V). No improvement was noticed in alkaline hydrolysis of the keto-ester (V), and on heating at high temperature the free acid finally esterified the product back to (V). It is allowed to react with ethyl α-bromopropionate according to Reformatsky. The reaction proceeds through an unusual course leading to cyclisation (Adamson, McQuillin, Robinson and Simonsen, *J. Chem. Soc.*, 1937, 1576). On alkaline hydrolysis of the reaction product and on esterification, it leads ultimately to (VI). It has, however, not been possible to separate the unsaturated keto-ester (VI) from the the unchanged material (V) through distillation. The presence of the unsaturated keto-ester (VI) in the reaction mixture is found to the extent of about 70% (λ^{alc}_{max}, 249 mμ; log ϵ=3.89) and the yield of the red 2:4-dinitrophenylhydrazone from the crude reaction mixture also supports this figure. An analytically pure sample of (VI), (λ^{alc}_{max}, 250 mμ; log ϵ=4.05) has been prepared through the decomposition of the red 2:4-dinitrophenylhydrazone with pyruvic acid (Mattox and Kendall, *J. Biol. Chem.*, 1950, **185**, 604). As this purification step will not be quite feasible with comparatively

large quantities of the Reformatsky product, it has been thought desirable to study the successive course of reactions with this impure ester (VI). Another reason for avoiding the purification step is that the red dinitrophenylhydrazone is found to be a mixture of derivatives of several stereoisomeric keto esters (V). On laborious fractional crystallisation, the melting point rose to 196-97° (Dutta *et al.*, *loc. cit.*). Most probably this may be the purer form of dinitrophenylhydrazone, described in the literature, melting at 178-83° (Gunstone and Tulloch, *loc. cit.*) or 185° (Abe *et al.*, *loc. cit.* 1953 *). The impure keto-ester (VI) is converted into enol acetate by refluxing with acetic anhydride and acetyl chloride, whereupon the absorption band at 249 mμ of the unsaturated ester in the ultraviolet has practically disappeared and in its place a new band at 238 mμ has appeared with high intensity. The enol-acetate is oxidised with permonophthalic acid in ethereal solution in the cold. The infra-red spectrum (Fig. 1) of the neutral material, isolated from the above oxidation, shows a strong hydroxyl band at 3μ and the αβ-unsaturated carbonyl band at 6μ, but no γ-lactone band at 5.7μ. In the ultraviolet region, it shows λ_{max}^{alc}, 235 mμ (log ε = 3.8). These results indicate that the epoxide ring has been already opened up with the elimination of β-hydroxyl group forming the αβ-unsaturated linkage, leading to the formation of (VII). The strong absorption band in the region 5.8μ is due to the carbomethoxyl groups in (VII) and (V) and of the carbonyl group of (V). To complete the isomerisation and to facilitate the formation of a lactone, the impure oxidation product (VII) is refluxed with potassium carbonate in aqueous methanolic solution. On distillation in high vacuum, a gummy mass is obtained and the infra-red studies (Fig. 2) of the neutral material indicate the presence of a dihydrosantonin to the extent of about 30%. The absorption band at 5.7μ is due to γ-lactone, at 6μ due to αβ-unsaturated carbonyl group of dihydrosantonin. Of the split-up band in the region 5.8μ, 5.78μ may be accounted for carbomethoxyl group and 5.82μ for the six-membered carbonyl group, the last two bands evidently arising from (V), present as an impurity in the hydroxy-ester (VII). On removal of the keto-ester (V) through alkaline hydrolysis in the cold, the neutral material shows very little tendency to solidify and from the ultraviolet studies (λ_{max}^{alc}, 247 mμ ; log ε = 3.9) it appears to consist mostly of dihydrosantonin. It forms readily an orange-red 1 : 4-dinitrophenylhydrazone. The stereochemical homogeneity cannot be definitely claimed, however, in this derivative although the analytical values are quite satisfactory. As it has not been possible to identify the hydroxy-ester (VII) because of its being contaminated with (V) or to isolate dihydrosantonin in a crystalline state, it has been thought desirable to characterise the oxidation product (VII) further through some of its reactions. It is known that systems of the type



* Dr. Abe has kindly identified it with the corresponding derivative of the keto-acid melting at 120° (*private comualcation*).

can be isomerised to the saturated 1 : 4-diketones with mineral acids (Ellis and Petrow, *J. Chem. Soc.*, 1939, 1078) or with alkalies (Herzig and Ehrenstein, *J. Org. Chem.*, 1951, **16**, 1050). With this expectation the impure hydroxy-ester (VII) was refluxed with methanolic hydrochloric acid resulting in the separation of a considerable amount of tarry matter. The ultraviolet studies of the crude reaction mixture indicate the presence of a strong absorption band at 294 mμ with considerable weakening of the original band at 245 mμ. Finally a low-boiling neutral product (IX) has been isolated and this is characterised by a doublet at 6.05μ and 6.15μ in the infra-red spectra. It forms a dark red 2 : 4-dinitrophenylhydrazone ($\lambda_{max}^{chlor\,f.}$ 408 mμ, log ϵ = 4.5 ; 315 mμ, log ϵ = 4.1). Recentiy Gunstone and Tulloch (*loc. cit.*) have described this dinitrophenylhydrazone melting at 251-53°. Dr. Gunstone was kind enough to compare the mixed melting point of the two samples and fonnd it as 256-60°, indicating the identical nature of both the products. The difference in melting point may be traced to polymorphism or our sample being purer. The ultraviolet maximum as recorded by us is at 408 mμ whereas Gunstone and Tulloch have recorded at 417 mμ. Our value compares favourably with the value (λ_{max}^{alc} 404 mμ) for β-cyperone-2 : 4-dinitrophenylhydrazone (McQuillin, *J. Chem. Soc.* 1951, 716 ; Roy, *Chem & Ind.*, 1954, 1393). Barton (*J. Chem. Soc.*, 1954, 3492) records λ_{max} at 415 mμ for the same derivative. On repeating the measurements, we have found that it is very difficult to identify the maximum as it is a broad spectrum between the regions 404 and 410 mμ, but on continued exposure to the ultraviolet, the absorption maximum gradually shifts to longer wave-length with the result that after two hours a maximum appears at 418 mμ. Again, search in the literature shows that dehydration in this type of ketol system under acidic condition has been reported (Romo *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 2918) even when the hydroxyl group occupies an equatorial position. In the present case, dehydration will be particularly facile because of the fact that the hydroxyl group occupies a more favoured axial position due to diaxial opening of the epoxide ring under the basic conditions des-

FIG. 1

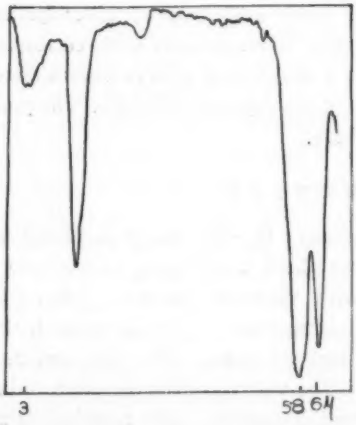
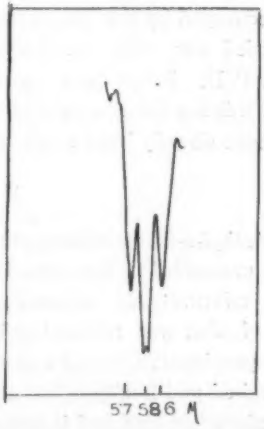


FIG. 2



cribed before (Barton, *J. Chem. Soc.*, 1953, 1033). Decarboxylation will, however, occur because of the presence of vinylogous β-keto-acid system (Clemo *et al.*, *ibid.*, 1946, 615).

Attempts at isomerisation under basic conditions with the expectation of obtaining (X) is of more immediate interest. This will supply not only an additional proof for the presence of γ-keto-allyl alcoholic system in the molecule but the diketo-acid is expected to serve as an important intermediate for the building up of *trans*-γ-lactone through preferential chemical reduction of the more hindered carbonyl group. This keto-lactone may be utilised directly for the synthesis of α- and β-santonin because methods for the building up of the dienone system through the action of bromine and bases have already been standardised in analogous cases by Inhoffen (*Ber.* 1943, **76B**, 233) and Wilds *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1712).

The structure of the diketo-acid reveals some of the interesting features in that each of the asymmetric centres excepting the C_9-carbon atom carrying the angular methyl group is adjacent to a functional group and is consequently epimerisable under ionisable conditions. In the stable configuration of the diketo-acid, C_4-methyl group and the propionic acid chain should be respectively α- and β- with respect to the angular methyl group. The ring junction should be *trans*. However, the isomerisation of C_{11}-methyl group in the propionic acid chain may not be so well defined in the open-chain acid, although it has been extensively studied in the corresponding lactones like α-santonin or desmotroposantonins (Woodward and Yates, *Chem. & Ind.*, 1954, 1391 and leading references ; cf. Dutta *et al.*, *loc. cit.*).

The hydroxy-ester (VII) is isomerised by refluxing with methanolic potassium hydroxide solution and the reaction has been followed by measuring the absorption at 245 mμ in the ultraviolet. The rearranged product is again refluxed with methanolic hydrochloric acid to remove any unisomerised material. The acidic product partly crystallises out, but purification has been found to be difficult and so it is directly esterified with diazomethane and the higher boiling fraction is converted into 2 : 4-dinitrophenylhydrazone. This on chromatographic purification affords yellow crystals, which correspond to the mono-dinitrophenylhydrazone of the diketo-ester (X).

Encouraged by the successful outcome of these experiments, investigations have been carried out with one of the stereochemically homogeneous acids corresponding to the ester (VI). It has been possible to isolate a dihydrosantonin of known stereochemistry and this has been correlated to santonin-D of the Japanese workers. The preliminary results have already been communicated elsewhere.

Experimental

2-Methyl-2-(β-carbethoxyethyl)-cyclohexanone (I).—To finely powdered sodamide (42 g.), suspended in dry ether (1200 c. c.), was added 2-methylcyclohexanone (112 g.), and the mixture was refluxed for 5 hours with vigorous stirring. After 2 hours the volume of ether was reduced to half and the mixture was cooled in an ice-bath. Ethyl β-bromopropionate (180 g.) was slowly added during ½ hour. The temperature was gradually raised and finally refluxed for 2 hours. The volume of the reaction mixture was again reduced to half and it was allowed to stand overnight. The reaction mixture was decomposed with ice and water and extracted with ether. The solvent was removed and

the residue was finally distilled, b. p. 160°-170°/30 mm., yield 125 g. To a solution of sodium (45.6 g.) in alcohol (600 c. c.), cooled in a freezing mixture, a cooled mixture of the above keto-ester (205 g.) and freshly distilled ethyl oxalate (255 g.) was added slowly, when a reddish brown solution was obtained. After standing overnight, the product was poured into ice-water and the neutral portion was extracted with ether. The alkaline portion was then acidified with cold dilute hydrochloric acid and the oily layer separating at the bottom was extracted with ether. The crude reddish oil, left after removal of the ether, was hydrolysed on the boiling water-bath with barium hydroxide (805 g.) and water (4020 c. c.) for 4 hours when the oil completely went into solution. The alkaline solution was then acidified and repeatedly extracted with ether after saturation with salt. The crude acid so obtained was finally esterified with EtOH (500 c. c) and H_2SO_4 (conc., 50 c. c.), previously mixed, by refluxing for 15 hours. The ester was worked up in the usual way and finally distilled, b p. 125°/3 mm., yield 160 g. (Found : C, 68.1 ; H, 9.6. $C_{12}H_{20}O_3$ requires C, 67.9 ; H, 9.4 per cent).

6-*Methyl*-6-(*β-carbethoxyethyl*-)-Δ^2-cyclo*hexenone* (II).—The keto-ester (I, 6g.) was dissolved in dry ether (100 c.c.) and cooled in ice-water. Dry bromine (1.6 c.c.) was added dropwise with shaking. On standing for an hour in the cold, the clear solution was poured into water and the ethereal layer separated, dried and distilled. The bromo-compound distilled at 145-50°/3 mm., yield 7.2 g. (Found : C, 50.8; H, 5.7. $C_{12}H_{19}O_3Br$ requires C, 49.4 ; H, 6.5 per cent).

The bromo compound (7.2 g.) was dehydrohalogenated by heating with quinoline (4.8 g.) at 150°-160° in an oil-bath for 15 minutes. It was cooled, diluted with ice-cold dilute HCl (1 : 1) and the dark oil was extracted with ether. The ethereal solution was again washed with alkali and acid and finally distilled when the unsaturated ester passed over at 120°-125°/3 mm., yield 4 g.

The 2 : 4-dinitrophenylhydrazone on repeated crystallisation from ethyl acetate separated in orange-red cubes, m.p. 92°. (Found : C, 55.02 ; H, 6.0 ; N, 14.6. $C_{18}H_{22}O_6N_4$ requires C, 55.3 ; H, 5.7 ; N, 14.3 per cent).

Ethyl 3-*Keto*-4-*methyl*-4-(*β-carbethoxyethyl*)-cyclo*hexylmalonate* (III).—To keto-ester (I, 150 g.) cooled in ice, was added dropwise dry bromine (48 c.c.) with shaking. In the beginning bromine was rapidly absorbed by the liquid and towards the end there was a copious evolution of HBr. After the addition was complete, it was allowed to stand in ice-water for half-an-hour. Next hydrogen bromide was removed first in water-suction and the last in vacuum. The bromo compound was mixed with freshly distilled pure quinoline (100 g.) and the mixture was heated in batches (about 30 g.) in an oil-bath at 150°-160° for 15 minutes and then rapidly cooled in tap-water. It was poured into excess of ice and H_2SO_4 (1 : 1). The dark brown reaction mixture was extracted with ether and the ethereal solution was washed with acid and alkali. The solvent was removed and the residue was distilled in vacuum. The unsaturated ester (91 g.) boiled at 120-25°/3 mm. and was contaminated to some extent with the saturated keto-ester (I), which formed a yellow 2 : 4 dinitrophenylhydrazone. Sodium (0.3 g.) was dissolved in absolute alcohol (80 c.c.) and to this was added ethyl malonate (70 g.) and the whole mixture was cooled to −5°. The above unsaturated ester (90 g.) in alcohol (30 c.c.) was similarly cooled and added and left at -5° for 6 hours and then

allowed to come to room temperature. It was decomposed with a little HCl and worked up in the usual way. After rejecting a little low-boiling fraction, the condensation product was collected at 195°-200°/0.7 mm., yield 120 g. (Found: C, 61.6; H, 8.1. $C_{19}H_{30}O_7$ requires C, 61.6; H, 8.1 per cent).

Ethyl 3-Keto-4-methyl-4-(β-carbethoxyethyl)-cyclohexylmethylmalonate (IV).—(*a*). Sodium (4 g.) was dissolved in absolute alcohol (120 c.c.) and the solution was cooled in a freezing mixture to -10°. The malonic ester derivative (60 g.), dissolved in alcohol (30 c.c.), was cooled to -10° and added to the sodium ethoxide solution. Alcohol (10 c.c.) was used for washing. The solution assumed a light yellow colour and it was allowed to stand at that temperature for half-an-hour. Methyl iodide (40 c.c.) was added and then the mixture was rapidly heated to boiling. After 4 hours' refluxing it was worked up in the usual way. The following fractions were collected: Fraction (i) 9g. (40°-50°/1 mm.); Fraction (ii) 12 g. (115-125°/1 mm.); Fraction (iii) 2 g. (130-185°/1 mm.) and Fraction (iv) 30 g. (190-195°/1 mm.). The last fraction corresponded to the desired ester. (Found: C, 62.6; H, 8.2. $C_{20}H_{32}O_7$ requires C, 62.5; H, 8.3 per cent). Fraction (ii) was the unsaturated ester (II), and this on condensation with ethyl malonate in the usual way yielded 35 g. of the ester (III).

(*b*). Sodium (0.2 g.) was dissolved in magnesium-dried alcohol (50 c.c.) and cooled to -5° in a freezing mixture. Ethyl methylmalonate (60 g.) was added with shaking and cooled to -5°. The above unsaturated keto-ester (II, 40 g.) in absolute alcohol (25 c.c.) was similarly cooled and was added dropwise with shaking to the above solution. After allowing the reaction mixture to stand at 0° overnight, it was acidified with cold dilute HCl and extracted with ether. The residue, left after removal of the ether, was distilled in vacuum. Unchanged ethyl methylmalonate passed over at 70°/10 mm. and next the unsaturated keto-ester at 120°-140°/5 mm. The desired condensation product passed over at 195°/0.5 mm., yield 43 g. (Found: C, 62.57; H, 8.36. $C_{20}H_{32}O_7$ requires C, 62.5; H, 8.3 per cent).

Methyl α-(3-Keto-4-methyl-4-β-carbomethoxyethylcyclohexyl)-propionate (V).—The above ester (IV, 94 g.) was mixed with acetic acid (630 c.c.) and HCl (conc., 240 c.c.) and refluxed for 5 days. The low-boiling products were removed in water-suction and the gummy residue was thoroughly dried and esterified with a mixture of methanol (400 c.c.) and H_2SO_4 (60 c.c.) by refluxing for 2 days. The product was worked up and the acidic fraction was reesterified, and finally the keto-dimethyl ester (56 g., 155-57°/0.5 mm.) was obtained. (Found: C, 62.8; 62.9; H, 8.2, 8.3. $C_{15}H_{24}O_5$ requires C, 63.4; H, 8.4 per cent). It could not be further characterised by any solid ketonic derivative.

Methyl α-(1: 2: 3: 5: 6: 7:8: 10-Octahydro-3-keto-4:9-dimethyl-6-naphthyl)propionate (IV).—The keto-ester (V, 18 g.) was mixed with ethyl α-bromopropionate (20 c.c.), benzene (50 c.c.) and zinc (10 g.) and the whole was refluxed after addition of a crystal of iodine. After an hour the reaction became vigorous. When the vigour of the reaction had subsided, another lot of ethyl bromopropionate (10 c.c.) and zinc (10 g.) was added and refluxing continued for an additional hour. The product was poured into ice-cold dilute HCl and worked up in the usual way. The low-boiling products were removed under suction in water pump and finally at 100°/5 mm. The residue was hydrolysed

with KOH (23 g.) in methanol (280 c.c.) by refluxing under nitrogen atmosphere for 4 hours. Methyl alcohol was removed and the solution was acidified and extracted with ether. The acidic fraction obtained on removal of the ether was dried and esterified with methanol (150 c.c.) and H_2SO_4 (conc., 15 c.c.) by refluxing for 8 hours. It was worked up and distilled in vacuum when the unsaturated ester (12 g.) passed over at 160°-170°/0.5 mm., which was contaminated with (V) to the extent of about 25-30%. The ester (1.7 g.) gave instantly a red 2 : 4-dinitrophenylhydrazone (2 g.), m.p. 150-55° which on twice crystallisation from ethyl acetate melted at 176-78°. (Found: C, 59.10; H, 6.3. $C_{22}H_{28}O_6N_4$ requires C, 59.4; H, 6.3 per cent). On laborious crystallisation of this derivative from ethyl acetate a fraction had been isolated as red fibrous crystals, m.p. 196-97°. (Found: C, 59.3; H, 6.3. $C_{22}H_{28}O_6N_4$ requires C, 59.4; H, 6.3 per cent). The 2 : 4-dinitrophenylhydrazone (1 g.) melting at 175-80° was dissolved in chloroform (10 c.c.) and warmed at 50°-60° under nitrogen with commercial pyruvic acid (10 g., 83-85%) and a solution of anhydrous hydrogen bromide in glacial acetic acid (1 c.c., 4*N*) for 6 hours. After dilution with chloroform and washing with sodium carbonate solution and water, the solvent was removed and the residue was distilled in high vacuum, whereupon a crystalline mass sublimed at about 100°/0.2 mm. and then the desired ester distilled at 165°/0.5 mm. The distillate was purified by passing through a column of alumina and washing down with petroleum ether containing a little benzene. The residue left after removal of the solvent was again evaporatively distilled in high vacuum. The desired ester passed over at 165°/0.5 mm. (Found: C, 72.3; H, 9.4. $C_{16}H_{24}O_3$ requires C, 72.8; H, 9.1 per cent).

Oxidation Experiments with Permonophthalic Acid: Formation of (VII) *and* (VIII).—The impure keto-ester (VI, 10 g.), obtained from the Reformatsky reaction, was refluxed with a mixture of acetic anhydride (50 c.c.) and acetyl chloride (50 c.c.) for 4 to 5 hours under nitrogen. The low-boiling fractions were removed in water suction and the residue was distilled in vacuum when the enol-acetate passed over at 155°-160°/0.7 mm. (yield 10 g.). It was oxidised with an ethereal solution (800 c.c., 0.8 g. of active oxygen per litre) of permonophthalic acid in the cold. After 5 days about two-thirds of the active oxygen was used up with copious separation of phthalic acid. The solution was washed with dilute sodium carbonate solution. The ethereal solution was washed thoroughly with water, dried with sodium sulphate and the solvent was completely removed and finally in vacuum, yield 7 g. The infra-red (Fig. 1) and ultraviolet studies indicate that the product consists mostly of (VII).

Attempts at preparation of a 2 : 4-dinitrophenylhydrazone did not lead to much success. The above hydroxy compound (VII, 3.5 g.) was refluxed for half-an-hour under nitrogen atmosphere with a solution of potassium carbonate (2.5 g.) in water (25 c.c.) and methanol (120 c.c.). The solution was cooled, acidified with acetic acid and thoroughly extracted with ether. The residue left after removal of the solvent was distilled in vacuum when a gummy mass (1 g.) passed over at 200°-210°/1 mm. This was dissolved in ether and the ethereal solution was washed with sodium carbonate solution to remove traces of acidic material and it was distilled again in high vacuum. The infra-red studies (Fig. 2) indicate the presence of a dihydrosantonin. To remove the keto-ester (V), which was most probably present, the gummy mass was treated

with methanolic potassium hydroxide (10 c.c., 10%) for 24 hours at room temperature. It was next acidified with acetic acid and on working up in the usual way, a neutral material (*ca.* 200 mg.) was collected, which was converted into 2:4-dinitrophenylhydrazone. It was crystallised from ethyl acetate in orange-red, small cubes, m. p. 231-32°. (Found: C, 58.9; H, 5.7. $C_{21}H_{24}O_8N_4$ requires C, 58.9; H, 5.6 per cent).

3-*Keto*-4:9-*dimethyl*-7-*ethyl*-1:2:3:7:8:9-*hexahydronaphthalene* (IX).—The impure hydroxy-ester (VII, 2 g.) was dissolved in methanol (100 c.c.) and fuming HCl (10 c.c.) was added and the solution was refluxed for 4 hours under nitrogen. It rapidly turned dark brown. The reaction was followed by studying the ultraviolet absorption at the end of every 2 hours. Next, the reaction mixture was diluted with water and extracted repeatedly with ether. The ethereal solution was washed with dilute NaOH solution and again washed with water. On distillation, a low-boiling oil (*ca.* 300 mg.) passed over at 100°-110°/0.7 mm., possessing a characteristic smell. It was directly converted into 2:4-dinitrophenylhydrazone, whereupon dark red flakes, separated out, m. p. 250-53°. This was purified through chromatography and the column of alumina was eluted with benzene, when the derivative crystallised out on concentrating the solution, m.p. 264-65°. (Found: C, 62.2; H, 6.0. $C_{29}H_{24}O_4N_4$ requires C, 62.5; H, 6.2 per cent).

Methyl α-(*Decahydro*-3:5-*diketo*-4:9-*dimethyl*-6-*naphthyl*)-*propionate* (X).—The impure hydroxy-ester (VII, 1.5 g.) was refluxed for 12 hours with a solution of KOH (6 g.) in water (50 c.c.). Next, it was acidified with acetic acid and evaporated in water suction. The residue was treated with acetone to extract the organic material. The residue, left after removal of the solvent, was again refluxed with HCl (conc., 5 c.c.) for 6 hours. The solution was evaporated to dryness and the residue was dissolved in methanol and esterified with diazomethane. The residue, left after removal of methanol, was distilled when a liquid (*ca.* 0.5 g.) passed over at 160°/0.4 mm. It was converted into 2:4-dinitrophenylhydrazone which separated as mixtures of two types of crystals, yellow and red. This was dissolved in benzene and allowed to pass through a column of alumina. On elution with benzene, a deep red solution was obtained in the beginning, the colour of which gradually turned yellow. On concentrating the latter fractions, yellow crystals separated which on recrystallisation from benzene melted at 234-35°. (Found: C, 57.8; H, 6.3. $C_{22}H_{28}O_7N_4$ requires C, 57.4; H, 6.1 per cent).

Grateful thanks are due to Dr. B. K. Bhattacharya and Dr. N.K. Bhattacharya for taking the I.R. spectra of a few samples in a double-beam infra-red spectrograph of Baird Associates Ltd. Some of the samples were analysed at Oxford (Dr. Weiler and Dr. Strauss) and a few samples at the Microchemical laboratory of the University College of Science, Calcutta by Mrs. Chhabi Dutta, M.Sc. Ultraviolet measurements were carried out with a Beckman spectrophotometer at the Bose Institute, Calcutta and with Hilgers "Uvispek" at the Inorganic Laboratories of the Association for which thanks are due to Mr. Amiya Kumar Chakravarti, M.Sc. Grateful thanks are also recorded to East India Pharmaceutical Works Ltd for a gift of Chemicals.

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CLAY MEMBRANE ELECTRODES FOR THE MEASUREMENT OF ZINC, MANGANESE AND COBALT ION ACTIVITIES

By D. K. Mitra and B. Chatterjee

Clay membrane electrodes have been developed for the measurement of zinc, copper, manganese and cobalt ion activities. The range of cation activity over which satisfactory results have been obtained is between 0.0001 and 0.0081 for Cu^{2+}, Mn^{2+} and Co^{2+} and between 0.0001 and 0.0243 for Zn^{2+}.

Clay membrane electrodes have so far been successfully used for the determination of ion activities of single cations, viz., ammonium (Marshall and Bergman, *J. Phys. Chem.*, 1942, **46**, 325), potassium (Marshall and Bergman, *J. Amer. Chem. Soc.*, 1941, **63**, 1911) ; sodium (Marshall and Krinbill, *ibid.*, 1942, **64**, 1814), calcium (Marshall and Ayers, *Soil Sci. Amer. Proc.*, 1946, **11**, 171), magnesium (Marshall and Eime, *J. Amer. Chem. Soc.*, 1948, **70**, 1302), barium (Chatterjee and Marshall, *J. Phys. Coll. Chem.*, 1950, **54**, 671) and copper (Mitra and Chatterjee, *J. Indian Soc. Soil Sci.*, 1953, **1**, 12). An attempt has been made in the present investigation to ascertain if clay membrane electrodes could be developed for measuring Zn, Mn and Co ion activities.

The clay membrane electrodes consist of small discs of clay films heated at the desired temperatures and fixed on the ends of pyrex glass tubings. A solution of known cation activity is placed inside the tube and the tube is then put in the solution under examination. The chemical cell under consideration can be illustrated as follows :

Calomel electrode	Sat. KCl	Solution of known cation activity (a_2)	Clay membrane	Solution of unknown cation activity (a_2)	Sat. KCl	Calomel electrode

The membrane acts as an ionic sieve, permeable to cations and not to anions. From a consideration of the membrane permeability theory, postulated simultaneously by Teorell (*Proc. Soc. Exp. Biol. Med.*, 1935, **33**, 382) and Myers and Sievers *Helv. Chim. Acta*, 1936, **19**, 649, 665, 987) and assuming that the density of the negative charge on the membrane is high, it can be shown that the equation for the total potential of the cell, illustrated above, reduces to the well known Nernst equation,

$$E = \frac{RT}{nF} \cdot \ln \frac{a_1}{a_2} \quad \ldots \quad \ldots \quad (1)$$

The details of the calculation have been presented in a previous publication (Chatterjee, this *Journal, Ind. & News Ed.*, 1949, **12**, 73 ; this *issue*, p. 739).

Experimental

Clay membranes or thin films of clay were prepared by careful evaporation at about 80° of 1.5 to 2.0% suspension of less than 0.5 micron fraction of the clay, saturated with the cation (Table I). The membranes, thus prepared, were cut into small discs (about 10 mm. in diameter) and heated for 24 to 48 hours at the desired temperature (Table I) in an electrically heated furnace. These membranes were then cemented on pyrex glass tubing and finally soaked in a fairly concentrated solution of the desired electrolyte to eliminate asymmetry potential. The particulars of the clay membranes have been detailed in Table I.

Table I

Membrane No.	Cation estimated.	* Clay isolated from	Membrane saturated with	Temp. of heating the membrane
Zn 1	Zinc	Padegaon-B	Calcium	600°
Zn 2	,,	,,	Hydrogen	700°
Zn 3	,,	Akli bentonite	Calcium	600°
Mn 1	Manganese	Padegaon-B	,,	700°
Mn 2	,,	,,	,,	600°
Mn 3	,,	Akli bentonite	,,	,,
Mn 4	,,	Tinpahari bentonite	,,	,,
Co 1	Cobalt	Padegaon-B	,,	500°
Co 2	,,	,,	,,	700°
Co 3	,,	Tinpahari bentonite	,,	600°

* All the clays are dominantly montmorillonitic.

The potentials of the cells were determined using two small calomel electrodes and the measured E. M. F. values compared with those calculated according to equation (1). The activity measurements are accurate to within 1 %.

The results so far obtained on the measurement of zinc, manganese and cobalt ion activities have been cited in Table II. The data showing the range of copper-ion activity over which satisfactory results have been obtained are taken from a previous publication (Mitra and Chatterjee, *loc. cit.*) and also presented in Table II for comparison.

TABLE II

Ion-activity measurements

[Mean experimental E. M. F. in millivolts].

Memb. No.	$a_{Zn^{2+}}$ ion. Inside. 0.0243	0.0243	0.0243	0.0243	0.0243
	Outside 0.0081.	0.0027.	0.0009.	0.0003.	0.0001.
1	14.4	28.4	42.4	56.0	72.0
2	14.8	29.0	42.6	56.2	69.0
3	14.0	27.8	40.6	54.0	68.0
Theoretical value	14.1	28.2	42.3	56.4	70.5

Memb. No.	$a_{Cu^{2+}}$ ion. Inside. 0.0243	0.0081	0.0027	0.0009	0.0003
	Outside 0.0081.	0.0027.	0.0009.	0.0003.	0.0001.
1	6.0	14.2	14.4	14.2	14.2
2	4.0	13.2	13.8	14.2	15.0
3	11.0	14.2	14.2	14 2	15.0
Theoretical value	14.1	14.1	14.1	14.1	14.1

Memb. No.	$a_{Co^{2+}}$ ion. Inside. 0.0243	0.0081	0.0027	0.0009	0.0003
	Outside 0.0081.	0.0027.	0.0009.	0.0003.	0.0001.,
1	8 0	14.2	14.0	14.2	16.0
2	3 4	11.8	12.0	13.0	16.0
3	0	11.2	11 0	14.2	16.0
Theoretical value	14.1	14.1	14.4	14.1	14.1

Memb. No.	$a_{Mn^{2+}}$ ion. Inside. 0.0243	0.0081	0.0027	0.0009	0.0003
	Outside 0.0081.	0.0027.	0.0009.	0.0003.	0.0001.
1	13.0	14.2	13.8	14.0	14.6
2	9.3	14.8	14 5	15.0	14.6
3	10.4	14.6	14.4	14.4	14 8
4	9.6	12.8	14.2	14.6	14.8
Theoretical value	14.1	14.1	14.1	14.1	14.1

The range of activity over which the Nernst equation is valid, depends on (*i*) the nature of the cation of which the activity is measured ; (*ii*) the nature of the cation saturating the membrane ; (*iii*) the clay mineralogical makeup of the membrane ; and (*iv*) the temperature of heating the membrane. Details of this aspect will be the subject matter of a subsquent publication. Taking the best membrane obtained, the range of cation activity over which satisfactory results have been obtained is between 0.0001 and 0.0081 for copper, manganese and cobalt and between 0.0001 and 0.0243 for zinc. Work on the activities of these cations in clay systems is in progress.

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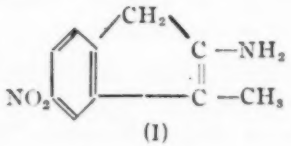
*iso*QUINOLINE DERIVATIVES. PART II

By T. N. Ghosh and Saktipada Dutta

In continuation of the previous work, (α-acetamido-β-*p*-chlorophenyl)-ethylmethyl ketone and the corresponding *o*-chloro analogue have been found to furnish, on the Bischler-Napieralski cyclisation, 1-methyl 7-chloro*iso*quinoline and the 5-chloro isomer respectively, the process involving cyclodehydration, dehydrogenation and deacetylation.

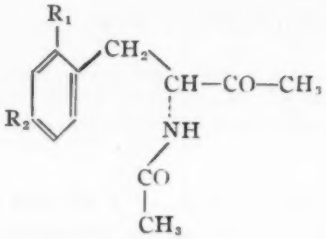
In Part I (Ghosh and Dutta, this *Journal*, 1955, **32**, 17) it has been shown that treatment of (α-acetamido-β-*p*-nitrophenyl)-ethylmethyl ketone with either concentrated sulphuric acid or with phosphorus oxychloride in nitrobenzene leads to the formation of 1-methyl-7-nitro*iso*quinoline, the process involving cyclodehydration, dehydrogenation and deacetylation. The possibilities of the formation in this reaction of an oxazole or a pyrazine derivative have been fully discussed in Part I (*loc. cit.*). However, another possibility, which was also considered but not recorded in Part I, concerns the formation of the indene derivative (I) in the present case, in analogy with the formation of 1-methylindene and 1-methylindene-2-carboxylic acid when benzylacetone and benzyl acetoacetic ester respectively are treated with concentrated sulphuric acid (Roser, *Ber.*, 1887, **20**, 1574 ; *Annalen*, 1888, **247**, 157). This possibility has also been eliminated on the ground that the compound under reference does not form any acetyl derivative nor does it condense with an aryl *iso*thiocyanate to form the corresponding thiocarbamide derivative, thereby showing the absence of an amino group.



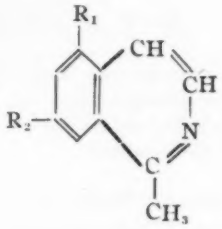
(I)

The above reaction provides the basis of a process leading to a facile formation of *iso*quinoline derivatives by the Bischler-Napieralski cyclisation and involves the use of a suitable acylamido ketone, the availability of which has been rendered possible in recent years by the general applicability of the Dakin and West reaction (*J. Biol. Chem.*, 1928, **78**, 91, 745, 757). For instance, although 7-chloro*iso*quinoline and the 5-isomer have been synthesised by Manske and Kulka (*Canadian J. Res.*, 1949, **27B**, 161), 1 methyl-7-chloro*iso*quinoline and the 5-chloro isomer do not appear to have been described in the literature. The synthesis of the latter compounds (IV and V) has now been effected by the treatment of (α-acetamido-β-*p*-chlorophenyl)-ethylmethyl ketone (II) and of the corresponding *o*-chloro analogue (III) respectively with either phosphorus oxychloride in nitrobenzene or with concentrated sulphuric acid. As in the case of the previous compounds, the formulations (IV and V) have been confirmed by (*a*) agreement with analytical figures, which are, however, incompatible with oxazole structures ; (*b*) absence of any amino group, which rules out the possibility of the formation of an amino-ketone or amino-indene derivative of the type (I) ; (*c*) strong basic character of the compounds ;

(*d*) absence of any ketonic property ; and (*e*) inertness towards dehydrogenation when treated with palladium-charcoal in tetralin at 240°-245°.



[II : R_1=H, R_2=Cl ; III : R_1=Cl, R_2=H]



[IV : R_1=H, R_2=Cl ; V : R_1=Cl, R_2=H]

Regarding the acylamido ketones, (II) and (III), required for the above syntheses in the penultimate stages, the preparation of (II) has previously been described (Ghosh and Dutta, this *Journal*, 1955, **32**, 725). By following a similar procedure, (α-acetamido-β-*o*-chlorophenyl)-ethylmethyl ketone (III) has now been prepared, thus : *o*-chlorobenzylbromide, obtained by bromination of *o*-chlorotoluene in presence of benzoyl peroxide, has been condensed with ethyl acetamidomalonate in presence of sodium ethoxide and the resulting ethyl α-carbethoxy-α-acetamido-β-*o*-chlorophenylpropionate hydrolysed by alkali to the corresponding dicarboxylic acid, which, when heated in presence of water, has readily furnished α-acetamido-β-*o*-chlorophenylpropionic acid. This mono-acid, when subjected to the Dakin and West reaction with acetic anhydride in presence of pyridine, has afforded (III).

The significance that is attached to these investigations is that, whereas the acylamidoketone, R—CH (NH—CO—CH_3)—CO—CH_3 (R=phenyl), when heated with concentrated sulphuric acid yields an oxazole derivative (Wiley, *J. Org. Chem.*, 1947, **12**, 43), the next higher homologue, namely, R-CH_2-CH (NH-CO-CH_3)-$COCH_3$ (R= phenyl or substituted phenyl), having a configuration which is apparently suited for the formation of either an oxazole or an *iso*quinoline derivative, however, affords on similar treatment an *iso*quinoline derivative with the elimination of the acetyl group and two atoms of hydrogen.

EXPERIMENTAL

Preparation of o-*Chlorobenzylbromide.*—Benzoyl peroxide (0.2 g.) (Kharasch *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 1405, used ascaridole for such a type of preparation, without, however, recording any experimental details) was added to a solution of *o*-chlorotoluene (40 g.) in CCl_4 (anhyd., 40 c. c.) and to this mixture, heated in diffused sunlight on a water-bath under reflux, a solution of bromine (64 g.) in CCl_4 (64 c.c.) was added dropwise. After the addition was over, heating was continued for about 7 hours to ensure complete bromination. The mixture was cooled and poured into cold water and requisite quantity of sodium bisulphite added to remove excess of bromine. The

CCl_4 layer was separated and the aqueous layer extracted twice with CCl_4 and the extracts were combined with the CCl_4 layer, and after washing with cold water the solution was dried. Removal of CCl_4 left a liquid (50 g.), b.p. 125°-130°/12 mm. (lit. b.p. 102°/9 mm.). (Found: Br, 39.3. C_7H_6ClBr requires Br, 38.9 per cent).

Ethyl α-Carbethoxy-α-acetamido-β-o-chlorophenylpropionate.—Ethyl acetamidomalonate (50 g.) was added to a cooled solution of sodium (4.5 g.) in anhydrous ethanol (125 c.c.) and the mixture shaken thoroughly when the ester went into solution. After addition of *o*-chlorobenzyl bromide (45 g.), the mixture was refluxed on the water-bath for about 10 hours. After distilling off ethanol under reduced pressure, the residual mass was cooled, treated with water and just acidified with hydrochloric acid. The solid was crystallised from ethanol in colorless plates (42 g.), m.p. 93-94°. (Found: N, 3.91. $C_{16}H_{20}O_5NCl$ requires N, 4.09 per cent).

α-Carboxy-α-acetamido-β-o-chlorophenylpropionic Acid.—The above ester (50 g.) was treated with aqueous caustic soda solution (10%, 300 c.c.) and the mixture heated on the water-bath for about 5 hours when the solid went into solution. The cooled solution was extracted with ether to remove any oily matter and the aqueous solution acidified with concentrated hydrochloric acid to Congo red. The precipitated solid (30 g.) was crystallised from ethanol (charcoal) in colorless rectangular plates, m.p. 147-48° (decomp.). (Found: N, 4.85. $C_{12}H_{12}O_5NCl$ requires N, 4.90 per cent).

That during the above hydrolysis the acetyl group has not been split off is supported by the observation of Snyder and Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 350) and of Ghosh and Dutta (this *Journal*, 1955, **32**, 17). Moreover, the above compound is insoluble in dilute hydrochloric acid and does not respond to any test for free amino group.

α-Acetamido-β-o-chlorophenylpropionic Acid.—A mixture of the above dicarboxylic acid (38 g.) and water (100 c.c.) was heated under reflux on the wiregauze till the evolution of carbon dioxide had ceased. The period required was about 3 hours. On cooling, a solid was obtained which was crystallised from water in colorless plates (20 g.), m.p. 166°. (Found: N, 5.92; chem. equiv., 238.5. $C_{11}H_{12}O_3NCl$ requires N, 5.79 per cent. Chem. equiv., 241.5).

(α-Acetamido-β-o-chlorophenyl)-ethylmethyl Ketone (III).—A mixture of α-acetamido-β-*o*-chlorophenylpropionic acid (25 g.), acetic anhydride (110 c.c.) and pyridine (85 c.c.) was refluxed on the water-bath for about 6 hours. Pyridine and the excess of acetic anhydride were removed by steam-distillation and the mixture cooled in ice. The separated solid was filtered, triturated with 5% aqueous sodium bicarbonate solution and finally crystallised from aqueous ethanol (1:1) in fine colorless needles (18 g.), m.p. 105-106°. (Found: N, 5.68. $C_{12}H_{14}O_2NCl$ requires N, 5.84 per cent).

2:4-*Dinitrophenylhydrazone* was crystallised from ethanol in yellow needles, m.p. 221-22°. (Found: N, 16.52. $C_{18}H_{18}O_5N_5Cl$ requires N, 16.68 per cent).

1-*Methyl-7-chloro*isoquinoline (IV).—A mixture of (α-acetamido-β-*p*-chlorophenyl)-ethylmethyl ketone (II: 10 g., prepared according to the method of Ghosh and Dutta, *loc.cit.*), $POCl_3$ (20 g.) and nitrobenzene (30 g.) was gradually heated under reflux in an oil-bath and the temperature of the bath was maintained at 175°-185° for about 12 hours. The mixture was cooled, treated with ice and water and then basified with 10% NaOH solution under cooling. After acidification with HCl (conc.), the

mixture was shaken twice with ether and the aqueous layer separated, filtered and basified with NaOH under cooling. The resulting alkaline solution was extracted with ether and removal of ether from the ethereal extract left a deep brown heavy liquid (5 g.), boiling at 280-82°/762 mm. (Found: C, 67.3; H, 4.6. $C_{10}H_8NCl$ requires C, 67.6; H, 4.5 per cent). It is a light yellow liquid with characteristic basic odour, being readily soluble in dilute mineral acids.

The *picrate* was readily formed in methanolic solution with a slight rise in temperature and crystallised from methanol in fine yellow plates, m.p. 146° (unaltered by further crystallisation). (Found: N, 13.9, 13.8. $C_{10}H_8NCl.C_6H_3O_7N_3$ requires N, 13.8 per cent).

The *chloroplatinate* was obtained as yellow needles, m.p. 193-94° (decomp.).

Action of Concentrated Sulphuric Acid on (II): *Formation of* (IV).—A solution of (II, 5 g.) in H_2SO_4 (25 c.c., *d* 1.84) was allowed to stand at room temperature for 2 hours, heated on a water-bath at 98°-100° for about 10 minutes, cooled and then poured into cold water, when there was a slight turbidity. After shaking thoroughly with ether, the clear solution was basified with NaOH solution and extracted with ether. On removal of the ether from the extract a deep brown liquid was left (readily soluble in dilute mineral acids), which was identified to be (IV) by the m.p. of the picrate and a mixed m.p.

1-*Methyl*-5-*chloro*isoquinoline (V).—A mixture of (III, 10 g.), $POCl_3$ (20 g.) and nitrobenzene (30 g.) was employed, following the procedure as described above, resulting in the isolation of (V, 4.5 g.), b. p. 280-82°/760 mm. It is a light yellow liquid, which is readily soluble in dilute mineral acids.

The *picrate* was obtained by warming a methanolic solution of the base with picric acid, cooling and scratching. It was crystallised from methanol in yellow plates, m. p. 118-19° (unaltered by further crystallisation). (Found: N, 13.7. $C_{10}H_8NCl.C_6H_3O_7N_3$ requires N, 13.8 per cent).

The *chloroplatinate* was obtained as yellow needles, m. p. 197-98° (decomp.).

Attempted Cyclisation of α-Acetamido-β-p-chlorophenylpropionic Acid.—In order to see whether this acid would furnish an *iso*quinoline derivative, the following procedure was adopted. In a flask protected from moisture P_2O_5 (37.2 g.) was treated with orthophosphoric acid (85%, 24 c. c.) and the mixture heated on a water-bath for 2 hours with occasional shaking (cf. Gilmore and Horton, *J. Amer. Chem. Soc.*, 1951, **73**, 1411). To this syrupy mass, when cooled, α-acetamido-β-*p*-chlorophenylpropionic acid (5 g.) and $POCl_3$ (7.5 c. c. Cf. Snyder and Werber, *loc. cit.*) were added and the mixture thoroughly shaken and then heated in an oil-bath at 125° for about 6 hours. After cooling, the mixture was treated with ice and water, when a flocculent precipitate was obtained which was filtered, crystallised from water and identified to be the original acid, m. p. and mixed m. p. 184° (cf. Ghosh and Dutta, *loc. cit.*). The filtrate, on basification with NaOH solution did not furnish any basic compound.

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REACTION OF THE ALKOXIDES OF SILICON, TITANIUM AND ZIRCONIUM WITH HYDROGEN BROMIDE

By Ram Charan Mehrotra

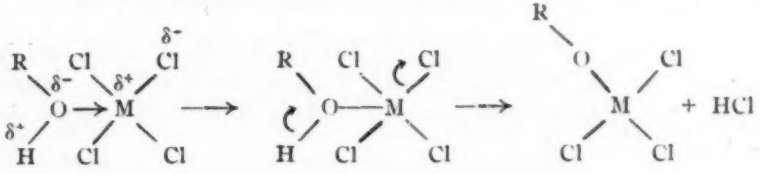
The reaction of hydrogen bromide with the alkoxides of silicon, titanium and zirconium has been studied. It has been found that butyl orthosilicate does not react with hydrogen bromide, titanium alkoxides yield dibromide derivatives and zirconium *iso*propoxide yields a mixture of zirconium mono *iso*propoxide tribromide and zirconium di-*iso*propoxide dibromide. The reactions provide methods for the preparation of these new compounds and demonstrate an interesting gradation in properties from silicon to zirconium.

In a recent communication (Mehrotra, this *Journal*, 1953, **30**, 731) it was shown that while butyl orthosilicate did not undergo any chemical change with hydrogen chloride, the alkoxides of titanium and zirconium were converted into chloride alkoxides according to the following reactions:

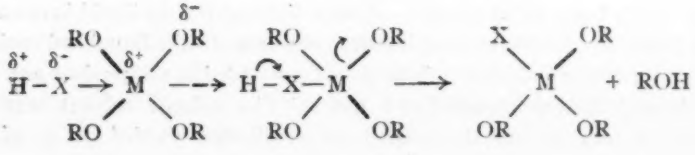
$$Ti(OR)_4 + 2HX \longrightarrow Ti(OR)_2X_2 + 2ROH$$
$$2Zr(OR)_4 + 5HX \longrightarrow Zr(OR)_2X_3 + Zr(OR)X_3 + 5ROH.$$

In view of the above, the corresponding reactions with hydrogen bromide have been studied and found quite similar. It has been possible to prepare the bromide alkoxides of titanium and zirconium, for the first time, by this method.

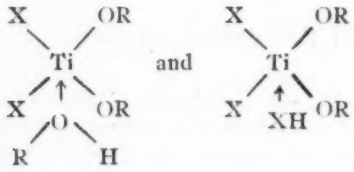
As suggested earlier (Bradley, Halim and Wardlaw, *J. Chem. Soc.*, 1950, 3450), the reaction between alcohols and titanium or zirconium tetrachloride occurs according to the following mechanism:



In view of the above, a similar mechanism can be suggested for the reaction between hydrogen halides and the tetra-alkoxides:



In the case of titanium, the electronic arrangement of the molecule Ti $OR)_2X_2$ is such that it canco-ordinate with an alcohol molecule or with a hydrogen halide molecule without the imposition of sufficient induced charges for a reaction of the above types to occur. It has been ob erved that under mild conditions both



can be sublimed, at least partially, unchanged. The gradation in the properties as we go from silicon to zirconium is very interesting and can be explained on lines similar to those offered by Bradley, Halim and Wardlaw (*loc. cit.*).

Experimental

n-Butyl orthosilicate, titanium ethoxide, *iso*propoxide and zirconium *iso*propoxide were prepared as described earlier (Bradley, Mehrotra and Wardlaw, *J. Chem. Soc.*, 1952, 2027, 4204, 5020; Mehrotra, this *Journal*, 1953, **30**, 731) and each alkoxide was purified carefully by the methods described.

Hydrogen bromide was prepared by the action of bromine on tetralin and the gas was purified by bubbling through tetralin to remove any accompanying bromine vapour.

Throughout these investigations, all-glass apparatus with interchangeable joints was employed and very careful precautious were taken to exclude moisture.

Silicon, titanium and zirconium were determined as the dioxides, and bromime, gravimetrically as silver bromide. It was, however, not possible to determine the alkoxy group by oxidation with potassium dichromate in these compounds as the hydrogen bromide interfered.

Reaction between n-Butyl Orthosilicate and Hydrogen Bromide

Hydrogen bromide gas was allowed to bubble briskly through distilled *n*-butyl orthosilicate (about 40 g., b.p. 115°/1.5 mm.). After a little while, the liquid became slightly warm and the passage of hydrogen bromide was continued till the liquid had cooled to the room temperature. Ethyl alcohol (about 50 g.) was added to the product and nitrogen was bubbled through the clear liquid for 2 hours. The volatile solvent was pumped off under reduced pressure and the product on distillation yielded 30 g. of *n*-butyl

orthosilicate, boiling at 115-16°/1.5 mm. [Found: Si, 8.83. Calc. for $Si(OBu)_4$: Si, 8.76 per cent). On raising the bath temperature, the distilling temperature went on rising and a little clear, transparent liquid (about 3 g.) distilled over at 160°-170°/1 mm.

If any reaction had occurred between hydrogen bromide and *n*-butyl orthosilicate with the formation of $SiBr(OBu)_3$, then it would have reacted with ethyl alcohol with the formation of the mixed ester $Si(OEt)(OBu)_3$. However, as the product consists mainly of *n*-butyl orthosilicate, it is obvious that no such reaction occurs. The small higher boiling fraction is probably hydrolysed silicon butoxide, $Si_2O(OBu)_6$, as the reaction between hydrogen bromide and butyl alcohol may produce traces of water.

Reaction between Titanium Tetra-ethoxide and Hydrogen Bromide

Dry HBr was bubbled through a solution of titanium tetra-ethoxide (16.8 g,, b.p. 121°/0.8 mm.) in benzene (30 c.c.). After about 3 to 4 minutes, the mixture became gradually hot and the passage of the gas was continued until the solution cooled down to the room temperature. The solvent was pumped off first on the water pump (20 mm.) and then the product was dried between 70° and 80° for 2 hours under 2 mm. pressure yielding 28.2 g. of a bright red viscous liquid. On analysis, the product was found to contain Ti, 11.7%; Br, 50.65%; Br:Ti, 2.6. On distillation of the product under reduced pressure, using glass wool, some decomposition was found to occur in the beginning, affording a reddish vapour which was condensed in the cold trap at −80° and was found to contain very little titanium. Finally, a red liquid distilled over at about 95°-105°/5 mm. The liquid solidified to furnish a red solid on cooling to the room temperature and analysed. [Found: Ti, 15.80; Br, 52.60; Br:Ti, 1.95. *Titanium dibromide diethoxide* $TiBr_2(OEt)_2$ requires Ti, 16.08; Br, 53.66 per cent].

Reaction between Titanium iso*Propoxide and Hydrogen Bromide*

The reaction between titanium *iso*propoxide and HBr was similar to above. Dry HBr was allowed to bubble through a solution of titanium *iso*propoxide (25.2 g.) in benzene (30 c.c.). Much heat was evolved and the passage of HBr was continued until the reaction mixture had cooled down to room temperature. From the product, volatile solvents were removed under reduced pressure and then the product was dried at 70°-80° for 2 hours under 2 mm. pressure, yielding 36.7 g. of a reddish yellow solid which analysed as Ti, 10.82%; Br, 49.0%; Br:Ti, 2.7. The product (35 g.) was distilled under reduced pressure using a capillary leak. Some brownish vapours came out first and finally a red liquid distilled over at 115°/4 mm. The liquid solidified to furnish a yellow solid (24 g.) which on analysis gave Ti, 13.48%; Br, 50.37%; Br:Ti, 2.24. On redistillation, again some decomposition appeared to occur and a yellowish liquid distilled over at 100°-102°/2.0 mm. affording a pale yellow solid which was analysed. [Found: Ti, 14.60; Br, 49.5; Br:Ti, 2.03. *Titanium dibromide di-*iso*propoxide* $Ti(OisoPr)_2Br_2$ requires Ti, 14.70; Br, 49.06 per cent].

Reaction between Zirconium isoPropoxide and Hydrogen Bromide

Dry HBr was briskly bubbled through a solution of zirconium *iso*propoxide [$Zr(O\textit{iso}Pr)_4.\textit{iso}PrOH$, 14.0 g.) in benzene (30 c.c.). Much heat was evolved and the passage of the gas was stopped after the reaction mixture had cooled down to the room temperature. Volatile solvents were taken off and the product was dried at 40°-50° under reduced pressure (1mm.) to afford a pale yellow solid which analysed for Zr, 20.7%; Br, 47.4% ; Br:Ti, 2.64. A mixture of $Zr(O\textit{iso}Pr)_2Br_2.\textit{iso}PrOH$ and $Zr(O\textit{iso}Pr)Br_3.\textit{iso}$-PrOH in the molar ratio of 1 : 2 requires Zr, 20.6% ; Br, 48.1%.

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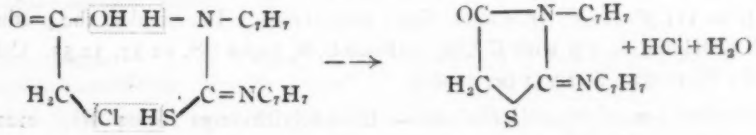
STUDIES ON 2-*m*- TOLYLIMINO-3-*m*-TOLYL-4-THIAZOLIDONE

By Prithwi Nath Bhargava and Girish Ch. Goswami

2-*m*-Tolylimino-3-*m*-tolyl-4-thiazolidone has been synthesised from *s*-di-*m*-tolylthiourea and monochloroacetic acid and its properties, degradation products as well as characteristic group reactions leading to various derivatives have been studied.

In view of the significant biological properties exhibited by 2 : 3-substituted-4-thiazolidones as inhibitors of electrically induced and metrazol-induced convulsions and local anaesthetics (Troutman and Long, *J. Amer. Chem. Soc.*, 1948, **70**, 3436; Surrey, *ibid.*, 1949, **71**, 3105, 3355), the preparations of some 2-arylimino-3-aryl-4-thiazolidones and their derivatives were taken up in these laboratories to provide them for biological studies (Bhargava, *ibid.*, 1951, **73**, 2353; Bhargava and Kaul, this *Journal*, 1955, **32**, 49). In continuation to the earlier work, 2-*m*-tolylimino-3-*m*-tolyl-4-thiazolidone has been prepared and its properties, degradation products as well as characteristic group reactions leading to various derivatives have been studied.

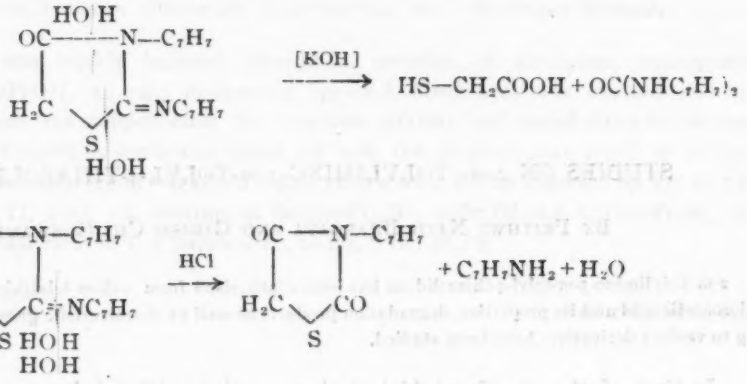
The compound in almost quantitative yield has been prepared by the interaction of *s*-di-*m*-tolylthiourea and monochloroacetic acid in presence of anhydrous sodium acetate and absolute alcohol under conditions laid down by Bhargava and Kaul (*loc. cit.*) according to the reaction :



(I)

The structure of the compound has been corroborated by its degradation products and characteristic derivatives obtained.

Thus, it has been found that the compound decomposes into *s*-di-*m*-tolylurea and thioglycollic acid when refluxed with a concentrated solution of alcoholic KOH and into 3-*m*-tolyl-2 : 4-thiazolidione and *m*-toluidine when boiled with alcoholic HCl, which can be explained as follows :



The reactive methylene group of the compound has been successfully condensed with nine aromatic aldehydes, one nitroso compound and one diazonium chloride to furnish a series of the corresponding 5-substituted thiazolidones.

The bivalent sulphur atom in the ring has been oxidised as in the previous paper (Bhargava and Kaul, *loc. cit.*) to furnish the sulphone derivative. Further, it has been found to form a hydrochloride.

EXPERIMENTAL

s-*Di*-m-*Tolylthiourea*.—A mixture of *m*-toluidine (0.046 *M*), CS_2 (0.054 *M*) and alcohol (6 c.c.) was refluxed on a water-bath for 1½ hours with 40% aq. KOH (2.5 c.c.) or 20% K_2CO_3 (12 c.c.). After distilling off the excess of EtOH and CS_2, the residue was washed with hot water, dilute HCl and water to remove unchanged alkali and *m*-toluidine. The recrystallised product from rectified spirit melted at 112°. Dyson record the m.p. as 111.5°-112.5° (*J. Chem. Soc.*, 1924, 1704). The yield of the product was 86% with KOH and 81.4% with K_2CO_3. (Found: N, 11.02 ; S, 12.53, 12.52. Calc. for $C_{15}H_{16}N_2S$: N, 10.93 ; S, 12.52 per cent).

2-m-*Tolylimino*-3-m-*tolyl*-4-*thiazolidone*.—s-Di-*m*-tolylthiourea (0.02 *M*), monochloroacetic acid (0.03 *M*), anhydrous sodium acetate (0.061 *M*) and absolute alcohol (25 c.c.) were refluxed together on a water-bath for 4 hours. After distilling off alcohol, the residue was washed several times with hot water to remove unchanged monochloroacetic acid and sodium acetate. The product recrystallised from absolute alcohol or preferably from benzene-alcohol mixture. m.p. 154°, yield 97.5%. (Found : N, 8.98, 9.24 ; S, 10.79. $C_{17}H_{16}ON_2S$ requires N, 9.46 ; S, 10.80 per cent).

After trial it was found that 4 hours' reflux of the reaction mixture gave the maximum yield.

Decomposition with KOH *into* s-*Di*-m-*Tolylurea and Thioglycollic Acid*.—A mixture of the thiazolidone (2.02 g.), *N*-alcoholic KOH (20 c.c.) and alcohol (15 c.c.) was refluxed on a water-bath for 3 hours and the contents then poured

into a large volume of water, and filtered. After washing it free of alkali, the residue was recrystallised from alcohol, m.p. 223°, yield 1.78 g. (92.5%). (Found : N, 11.42. $C_{15}H_{16}ON_2$ requires N, 11.66 per cent).

That the above product was *s*-di-*m*-tolylurea, was confirmed by its further hydrolysis with alcoholic HCl to *m*-toluidine, characterised by the azo-β-naphthol dye, m.p. 140°.

The original filtrate gave a purple colour with sodium nitroprusside solution and a greenish blue colour (characteristic of thioglycollic acid) when $FeCl_3$ was added to a HCl-acidified part.

Hydrolysis with Alcoholic HCl *to* 3-m-*Tolyl*-2 : 4-*thiazolidione and* m-*Toluidine.*—The thiazolidone (2 g.), rectified spirit (15 c.c.) and HCl (conc., 6 c.c.) were refluxed on a water-bath for 6 hours. After distilling off alcohol, the thiazolidione was extracted with boiling water. The extract after concentration and cooling was left overnight for complete crystallisation. The product was recrystallised from hot water, m.p. 90°, yield 0.2 g. (14.3%). (Found : S, 15.48. $C_{10}H_9O_2NS$ requires S. 15.45 per cent).

The presence of *m*-toluidine hydrochloride in the extract after removal of crystallised thiazolidione was confirmed by its azo-β-naphthol derivative, m.p. 140°.

Condensation with Aldehydes and α-*Nitroso*-β-*naphthol* : *Formation of* 5-*Arylidene and* 5-*Arylimino Derivatives.*—These condensations are summarised in Table I. The aldehydes and α-nitroso-β-naphthol were always taken slightly in excess of the required molar quantity. In the case of solid and liquid aldehydes having b.p. higher than 150°, solvent was found to be unnecessary. Where such attempts failed to afford good results, solvents were used in very small quantities.

TABLE I

2-m-*Tolylimino*-3-m-*tolyl*-5-(*substituted*)-4-*thiazolidone.*

Nature of the compound condensed.	Cond. agent.	Refluxed for.	at.	Yield.	Recryst.	Colour.	M.P.	% Sulphur. Found.	Calc.
Benzaldebyde	...	6 hrs.	150°	86.0%	a	Pale yellow	175-76°	8.36	8.34
m-Nitrobenzaldehyde	x	6	100°	71.3	a	Yellow	208°	7.48	7.47
o-Nitrobenzaldehyde	y	7	150°	41.4	ba	Do	164°	7.49	7.47
m-Hydroxy-benzaldehyde	y	7	100°	43.0	c	Pale yellow	169°	8.09	8.01
Cinnamaldehyde	..	7	150°	54.2	a	Yellow	184°	7.87	7.82
Anisaldehyde	...	7	150°	47.9	d	Pale yellow	182°	7.73	7.74
Salicylaldehyde	...	7	150°	48.1	a	Yellow	235°	8.06	8.01
Vanillin	x	8	150°	68.84	a	Do	220°	7.42	7.45
Piperonal	x	8	150°	55.34	a	Dirty yellow	252°	7.47	7.49
α-Nitroso-β-naphthol	x	5	150°	59.06	c	Black	230°	7.14	7.11

x, alcohol and anhydrous sod. acetate ; y, pyridine.

a, dissolved in chloroform and reprecipitated by alcohol in cold ; ba, derivative extracted with hot petroleum ether and recrystallised as in a ; c, rectified spirit ; d, dissolved in chloroform and reprecipitated by petroleum ether in cold.

2-m-*Tolylimino*-3-m-*tolyl*-5-(p-*sulphonamidophenylazo*)-4-*thiazolidone*.—To an ice-cold solution of sulphanilamide (1 g.) in glacial acetic acid (10 c.c.) containing HCl (conc., 1.5 c.c.) and sodium acetate (4 g.), sodium nitrite (2.5 g.) was added slowly within 15 minutes. After another 15 minutes, a solution of the thiazolidone (1.5 g.) in glacial acetic acid (15 c.c.) was added to it gradually. After half an hour the solution was diluted and allowed to stand overnight. The scarlet-red derivative was recrystallised from chloroform, m.p. 235° (decomp.), yield 61.8%. (Found: S, 13.24. $C_{23}H_{21}O_3N_5S_2$ requires S, 13.37 per cent).

2-m-*Tolylimino*-3-m-*tolyl*-4-*thiazolidone*-1-*dioxide* was prepared by the method of Troutman and Long (*J. Amer. Chem. Soc.*, 1948, **70**, 3436), slightly modified as described below.

To a solution of the thiazolidone (1 g.) in glacial acetic acid (15 c.c.), H_2O_2 (20 vol., 30 c.c.) was added and the precipitated thiazolidone was redissolved by adding acetic anhydride (20 c.c.). The temperature of the mixture was slowly raised to 55° on a water-bath. At this point the flask was intermittently cooled to keep the temperature below 60°. When the evolution of heat had apparently ceased, the solution was allowed to stand for 48 hours at room temperature. The excess of the solvent was then removed by distillation under reduced pressure at 65°. The residue was mixed with 50% alcohol and heated for sometime. The resinous mass, separated on cooling, was extracted with benzene, and the extract was washed free of acid in a separating funnel. After evaporation of the benzene, the resinous mass was dissolved in chloroform-alcohol mixture and left for two days. The brown-coloured sulphone crystallising out melted at 214°, yield 54.15%. (Found: S, 9.74. $C_{17}H_{16}O_3N_2S$ requires S, 9.76 per cent).

2-m-*Tolylimino*-3-m-*tolyl*-4-*thiazolidone Hydrochloride*.—The thiazolidone (1 g.) was dissolved in dry benzene (15 c.c.), taken in a 50 c.c. conical flask, and dry HCl gas was passed through the solution. A gummy precipitate separated out, which became crystalline on standing overnight. On recrystallisation from benzene, a white crystalline product, m.p. 180-82°, was obtained. (Found: C, 61.26; H, 5.13; N, 8.46; S, 9.68; HCl, 10.92. $C_{17}H_{16}ON_2S$. HCl requires C, 61.35; H, 5.11; N, 8.42; S, 9.62; HCl, 10.97 per cent).

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A STUDY OF INFRA-RED ABSORPTION SPECTRA OF STAPHISINE AND A NEW ALKALOID

By Sharda Dasgupta and Bhola Nath

The infra-red absorption spectra of staphisine and new a base, isolated from *Delphinium staphisagria* have been examined. In staphisine a hydroxyl group is detected to be involved in H-bonding, and the possible existence of a conjugated double bond (C=C) is indicated. It appears to occur in a dimolecular form and the view held hitherto, that there is a resistant double bond in the molecule, does not seem to be plausible.

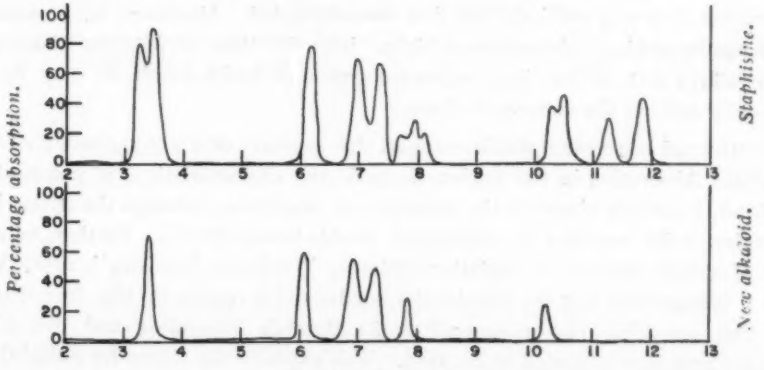
In *Delphinium staphisagria* L., staphisine (Jacobs and Craig, *J. Biol. Chem.*, 1941, **141**, 67) and a new alkaloid (Clemo and Nath, *J. Chem. Soc.*, 1952, 1751) occur along with delphinine (Henry, "Plant Alkaloids", 1949, p. 697), and these have been isolated from the mother-liquors of delphinine.

The molecular formula and functional groups of staphisine have not been characterised ; only an N-methyl group could be recognised. On the basis of chemical evidence and ultraviolet absorption study, it has not yet been possible to establish the character of the oxygen atom as well as the degree of unsaturation in the staphisine molecule. Regarding the new base, beyond the fact that it yields a phenanthrene derivative on selenium dehydrogenation, nothing is reported in literature. As infra-red absorption bands are diagnostic of functional groups in many respects, the spectra of staphisine and the new base have been examined and some useful information is embodied in this communication.

The infra-red absorption spectra are shown in Fig. 1 as percentage absorption *vs* wave-length. It was recorded with a Grubb Parsons single beam instrument (NaCl optics : powder spectra).

FIG. 1

Infra-red absorption spectra.



Staphisine.—The strong band at about 3.24μ indicates the presence of a hydrogen bonded hydroxyl group. The intense band near 6.19μ indicates a system of conjugated double bonds (C=C). The strong band at 7.32μ suggests the presence of >N-Me group. Besides these, the spectrum contains strong bands at 3.43μ, 6.94μ and 7.32μ also which could be due to $>CH_2$ and/or $-CH_3$ groups.

The New Base.—The intense band at 3.43μ and medium ones at 6.94μ and 7.32μ also indicate the presence of $>CH_2$ and/or $-CH_3$ groups. The band at 7.32μ may also be interpreted as due to >N-Me group. The weak band near 10.22μ indicates the presence of *trans* double bond (CH=CH). There is a medium band at 6.08μ and a weak one at 7.85μ, which may be due to the presence of C=O and -OMe groups respectively.

DISCUSSION

(*a*) **H-*bonding*.**—Absorption in the region 9.10μ to 7.69μ, which is indicative of ordinary type of OH groups, is absent in the staphisine spectrum, whereas the band observed at about 3.24μ indicates the presence of a hydroxyl group involved in H-bonding. This group appears to have formed a fairly stable chelate ring as a result of the combination of two molecules of staphisine.

(*b*) *Conjugated double bonds.*—Staphisine is thought to be an equilibrium mixture of a simple base and its dimolecular condensation product (Manske and Holmes, "The Alkaloids" IV, p. 289, 1954):

$$2C_{21}H_{31}ON \rightleftharpoons C_{42}H_{60}ON_2 + H_2O.$$

On catalytic hydrogenation, it consumes only one mole of hydrogen, but two forms of a tetrahydro derivative corresponding to the dimolecular formula are obtained. The ultraviolet absorption curve exhibits a maximum at 2670Å (*ε-ca.*, 10,000), which may indicate the presence of two homoannular conjugated ethylenic linkages. If staphisine be assumed to have been derived from the hypothetical pentacyclic $C_{19}H_{27}NH$ nucleus (Manske and Holmes, *loc. cit.*), the monomeric form, $C_{21}H_{31}ON$, should contain two ethylenic linkages. But as one of these two linkages has been observed to be resistant to hydrogenation, it is very unlikely that they are conjugated. Moreover, such conjugation would normally produce absorption of higher intensity than is actually observed. It therefore follows that, if there is a conjugated system of double bonds, it may be due to a dimolecular and not the monomeric form.

The infra-red absorption studies support the presence of a conjugated double bond system thus: Absorption in the region 6.02μ-6.04μ, characteristic of a non-conjugated double bond, is entirely absent in the spectrum of staphisine, whereas the strong band at 6.19μ indicates the presence of conjugated double bonds (C=C). Further, on a consideration of certain features of chelation (Gilman, "Organic Chemistry", 1938, Vol. II, p. 1643) it is suggested that the dimolecular condensation results in the formation of a chelate ring involving two monomeric units through H-bonding and two ethylenic linkages are present conjugated in the ring. This explains the reason for a slightly lower value of the ultraviolet absorption intensity and also the formation of tetrahydro

derivatives of the dimolecular form on hydrogenation. However, at this stage, it is not possible to ascertain the number of members of the chelate ring, but it is certainly not less than six.

(*c*) *Methylimino Group.*—The strong band at 7·32μ confirms the presence of a >N-Me group which has been chemically established (Jacobs and Craig, *loc. cit.*). This group is not likely to be a member of the chelate ring system ; consequently there may not be any association of points of unsaturation with the nitrogen atom as postulated by Jocobs and co-workers (*J. Biol. Chem.*, 1944, **154**, 293) in their hypothetical tetracyclic structure of certain alkamines related to staphisine.

(*d*) *The Problem of Resistant Double Bonds.*—Jacobs and Craig (*loc. cit.*) have assumed the presence of a resistant double bond in the staphisine molecule in order to explain the absorption of one mole of hydrogen and the ultraviolet intensity equivalent to a conjugated system of olefinic double bonds. But our infra-red absorption study disposes of the idea of resistant double bonds in it, and in addition indicates that the molecule is of dimolecular form, $C_{42}H_{60}ON_2$, containing two double bonds in conjugation within a chelate ring.

(*e*) *Comparison of Structural Features of Delphinine with those of Staphisine and the New Base.*—Although staphisine and the new base have been found to occur along with the delphinine alkaloid in *D. Staphisagria* seeds, there appears to be little in common in their infra-red absorption. Delphinine (Nath, this *Journal*, 1955, **32**, 75) possesses a non-conjugated double bond, but staphisine shows the presence of conjugated ethylenic linkages. Chelation too is of different character in both. The spectra, thus, indicate some deep-seated differences in their structures. It is quite likely that because of such differences in their structures, staphisine and the new base have yielded, on selenium dehydrogenation, phenanthrene homologues, indicating their relationship to a diterpenoid, whereas delphinine gave a hydrocarbon belonging to a different category (Jacobs and Huebner, *J. Biol. Chem.*, 1947, **170**, 209).

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SYNTHESIS IN ACRIDINE SERIES. PART II

By S. R. Patel and K. S. Nargund*

5-(δ-Diethylamino-α-methylbutyl)amino and similar other 5-*N*-substituted-amino derivatives of 3:7-dichloro- and 3:9-dichloro-acridines have been synthesised by cyclisation of the corresponding amides of the 4:4′-dichloro- and 4:2′-dichloro-diphenylamine-2-carboxylic acids respectively.

The importance of a chlorine atom as a contributory factor towards the antimalarial property is well established in case of antimalarials of the acridine and the quinoline series. Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1596) have reported that 2:8-dichloro-5-(δ-diethylamino-α-methylbutyl)aminoacridine (I) has quinine equivalent of 5.0 when tested therapeutically against *P. gallinaceum* infections in chicks; in the same test atebrine has Q. E. of 1.3. Compound (I) contains two chlorine atoms, both in positions *meta* to ring-nitrogen, while atebrine contains only one chlorine atom in a similar position in its molecule. The increased activity of (I) is probably due to the additional chlorine atom. In order to ascertain whether other dichloro-5-N-substituted acridine derivatives possess therapeutic properties similar to those of (I), the synthesis of 3:9- and 3:7-dichloro-5-N-substituted aminoacridines was undertaken.

2:5-Dichlorobenzoic acid (Nargund *et al.*, this *Journal*, 1947, **24**, 373) was condensed with *o*-chloroaniline to obtain 4:2′-dichlorodiphenylamine-2-carboxylic acid in about 80% yield. However, when the reaction was carried out at a low temperature using *iso*amyl alcohol, the yield was very poor. The acid chloride, obtained by treating the above acid with thionyl chloride, was then allowed to react with the required amine to yield the corresponding amide. The amide was then directly cyclised to 3:9-dichloro-5-N-substituted aminoacridine derivative by treating it with phosphorus oxychloride.

Following a similar method, 3:7-dichloro-5-N-substituted aminoacridine derivatives were prepared, starting with 4:4′-dichlorodiphenylamine-2-carboxylic acid which was obtained by Ullmann's condensaition of 2:5-dichlorobenzoic acid with *p*-chloroaniline.

The 5-N-substituted aminoacridine derivatives have been isolated as hydrochlorides. The corresponding bases were obtained as somewhat sticky yellow solids and could not be crystallised properly.

Experimental

4:2′-Dichlorodiphenylamine-2-carboxylic Acid.—A mixture of 2:5-dichlorobenzoic acid (10 g.), potassium carbonate (1 g.), nitrobenzene (30 c.c.) and benzene (8 c.c.)

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3—1890P—12

TABLE I

[DH denotes dihydrochloride and DP, dipicrate]

Amino compound used.	Product obtained.	M.P.	Found %Cl.	Found %N.	Formula	Calc. %Cl.	Calc. %N.
γ-Diethylamino-propylamine	3:7-Dichloro-5-(γ-diethyl-aminopropyl)-aminoacridine DH	237-39°	31.9	9.5	$C_{20}H_{25}N_3Cl_4$	31.6	9.3
γ-Morpholino-propylamine	3:7-Dichloro-5 (γ-morpholino-propyl)aminoacridine DH	236°	31.0	9.3	$C_{20}H_{23}ON_3Cl_4$	30.8	9.1
γ-Piperidino-propylamine	3:7-Dichloro-5-(γ-piperidino-propyl)aminoacridine DH	243-45°	31.6	9.4	$C_{21}H_{25}N_3Cl_4$	30.8	9.1
δ-Diethylamino--α-methylbutylamine	3:9-Dichloro-5 (δ-diethyl-amino-α-methylbutyl)-aminoacridine DP	202-205°	8.6	14.9	$C_{34}H_{33}O_{14}N_9Cl_2$	8.2	14.6
γ-Diethylamino-propylamine	3:9-Dichloro-5-(γ-diethyl-amino-α-methylbutyl)-aminoacridine DP	185-87°	8.7	15.4	$C_{32}H_{29}O_{14}N_9Cl_2$	8.5	15.1
γ-Morpholino-propylamine	3:9-Dichloro-5-(γ-piperidino-propyl)aminoacridine DH	245°	31.0	9.3	$C_{21}H_{25}N_3Cl_4$	30.8	9.1
γ-Piperidino-propylamine	3:9-Dichloro-5-(γ-morpholino-propyl)aminoacridine DH	242°	31.1	9.4	$C_{20}H_{23}ON_3Cl_4$	30.8	9.1

N.B.: (*i*) All the hydrochlorides have been obtained as yellow crystalline powders from alcohol-acetone mixture.
(*ii*) The products melt with decomposition.
(*iii*) The dipicrates have been crystallised from alcohol in small yellow needles.

was refluxed at 100° for half an hour. Benzene was then distilled off, which removed the traces of water formed during the formation of the potassium salt of the acid. *o*-Chloroaniline (7 g.) and a trace of Cu powder were then added to it and then the temperature was raised to 165°-180° and heating was continued for 3 hours more. The reaction mixture was then filtered. The filtrate on acidification furnished 4:2′-dichlorodiphenylamine-2-carboxylic acid as a green powder. It crystallised from hot acetic acid in small yellow needles, m.p. 234°, yield 8 g. (Found: Equiv., 280; N, 4.8; Cl, 25.6. $C_{13}H_9O_2NCl_2$ requires equiv., 282; N, 4.9; Cl, 25.2 per cent).

4:2′-*Dichlorodiphenylamine-2-carboxylic Chloride.*—The above acid (2 g.) was heated with thionyl chloride (4 c. c.) on a water-bath till dissolution. Excess of thionyl chloride was then removed by distillation and the yellow solid remaining behind was crystallised from petrol-ether in small yellow needles, m.p. 142-45°, yield 1.5 g. (Found: N, 4.5; Cl, 35.8. $C_{13}H_8ONCl_3$ requires N, 4.6; Cl, 35.4 per cent).

4:4′-*Dichlorodiphenylamine-2-carboxylic acid* was obtained, as indicated above, by condensing 2:5-dichlorobenzoic acid with *p*-chloroaniline using the reactants in the same proportions. It crystallised from acetic acid in small yellow needles, m.p. 227-29°, yield 8.5 g. (Found: Equiv., 279; N, 4.75; Cl, 25.4. $C_{13}H_9O_2NCl_2$ requires equiv., 279; N, 4.9; Cl, 25.2 per cent).

4:4′-*Dichlorodiphenylamine-2-carboxylic chioride* was obtained from the above acid by treating it with thionyl chloride, as indicated above. It crystallised from petrol-ether in small yellow needles, m.p. 134-35°. (Found: N, 4.5; Cl, 35.9. $C_{13}H_8ONCl_3$ requires N, 4.6; Cl, 35.4 per cent).

3:7-*Dichloro*-5-(δ-*diethylamino*-α-*methylbutyl*)*aminoacridine Hydrochloride.*— The method described here is typical for the synthesis of other analogous derivatives described in this paper.

4:4′-Dichlorodiphenylamine-carboxylic chloride (1.5 g.) was dissolved in dry benzene (10 c.c.) and to this solution δ-diethylamino-α-methylbutylamine (1.2 g.) was added and the mixture was refluxed for an hour. $POCl_3$ (3 c.c.) was then added and heating was continued for 2 hours more. Excess of benzene was then distilled off and the product was decomposed with ice and ammonia solution. The yellow sticky base which separated was extracted with dilute acetic acid solution. The acetic acid extract was decomposed with ammonia and the base separating was extracted with ether. The ether extract was dried and alcohol, saturated with dry HCl, was added to it to precipitate the hydrochloride as a yellow solid. It was then crystallised from alcohol-acetone mixture (1:1) as yellow granules, m.p. 254°. (Found: N, 9.0; Cl, 30.1. $C_{22}H_{29}N_3Cl_4$ requires N, 8.8; Cl, 29.8 per cent).

Other similar 5-N-substituted derivatives of 3:7-dichloro- and 3-9-dichloro-acridines are described in Table I.

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THE FRIES REARRANGEMENT OF 4-METHYL-7-COUMARINYL BENZENESULPHONATE

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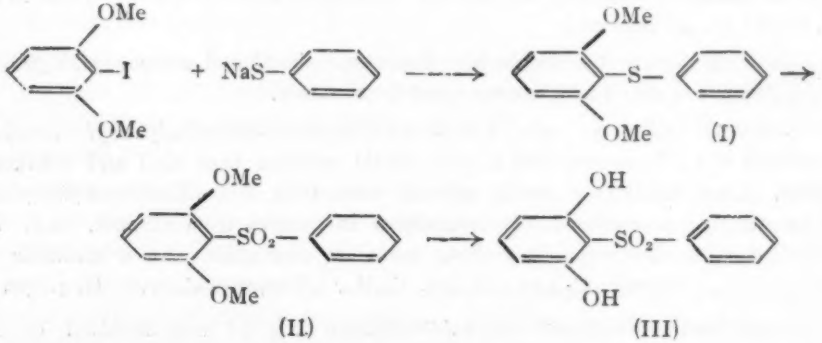
4-Methyl-7-coumarinyl benzenesulphonate isomerises to 7-hydroxy-4-methyl-8-phenylsulphonylcoumarin on heating with anhydrous aluminium chloride. If the isomerisation is effected in nitrobenzene solution, the product is a mixture of 7-hydroxy-4-methyl-6- and -8-phenylsulphonylcoumarins.

In extension of our studies on the Fries isomerisation of aryl sulphonates (*Curr. Sci.*, 1953, **22**, 307; this *Journal*, 1954, **31**, 513), the isomerisation of 4-methyl-7-coumarinyl benzene- and *p*-toluene-sulphonates was undertaken. While the work was in progress, Bhavsar and Desai (this *Journal*, 1954, **31**, 167) published their work on 4-methyl-7-coumarinyl *p*-toluenesulphonate, the results agreeing with ours. We therefore describe here the rearrangement of 4-methyl-7-coumarinyl benzenesulphonate.

4-Methyl-7-coumarinyl benzenesulphonate did not isomerise below 80°; at 120°-130° without a solvent, it isomerised to the extent of 17%, furnishing 7-hydroxy-4-methyl-8-phenylsulphonylcoumarin along with a considerable quantity of the monochloro derivative of 7-hydroxy-4-methylcoumarin, reported by Bhavsar and Desai (*loc. cit.*). The chloro compound melted at 270°, its acetate melting at 188-89°. It was found to be identical with 8-chloro-7-hydroxy-4-methylcoumarin (Chakravarti and Ghosh, this *Journal*, 1935, **12**, 791). When the isomerisation of 4-methyl-7-coumarinyl benzenesulphonate was effected in nitrobenzene, the chloro compound was completely absent; the product was then a mixture of 7 hydroxy-4-methyl-6- and -8-phenylsulphonylcoumarins.

The structure of 7-hydroxy-4-methyl-8-phenylsulphonylcoumarin followed from the fact that it underwent alkaline cleavage, affording 2:6-dihydroxydiphenylsulphone (III), the structure of which in turn was established by an unambiguous synthesis as shown below:



The identity of 7-hydroxy-4-methyl-6-phenylsulphonylcoumarin was established by preparing it from 2:4-dihydroxydiphenylsulphone and ethyl acetoacetate by the Pech-

mann condensation. Proof of the structure of 7-hydroxy-4-methyl-6-*p*-toluenesulphonylcoumarin (Bhavsar and Desai, *loc. cit.*) was also obtained from a similar synthesis.

EXPERIMENTAL

The Fries Rearrangement of 4-Methyl-7-coumarinyl Benzenesulphonate in the absence of a Solvent.—A mixture of the sulphonate (6.4 g.) and powdered $AlCl_3$ (anhydrous, 10.6 g.) was heated at 120°-130° for 45 minutes. It was cooled, treated with HCl (dil.) and filtered. The precipitate was washed with water and extracted several times with a saturated solution of sodium bicarbonate. The extract on acidification furnished a mixture of two substances, one of which was soluble in cold benzene. The benzene-insoluble portion (2.50 g.) on recrystallisation from ethanol melted at 270°. It afforded an acetate of m.p. 188-89°, and was found to be 8-chloro-7-hydroxy-4-methylcoumarin (Chakravarti and Ghosh, *loc. cit.*). The benzene-soluble portion (0.50 g.) crystallised from benzene in needles, m.p. 220-21°. (Found : C, 60.5; H, 4.0. $C_{16}H_{12}O_5S$ requires C, 60.75 ; H, 3.8 per cent). The compound was identified as 7-hydroxy-4-methyl-8-phenylsulphonylcoumarin (*vide infra*).

The Fries Rearrangement of 4-Methyl-7-coumarinyl Benzenesulphonate in Nitrobenzene.—To a solution of the sulphonate (12.6 g.) in nitrobenzene (60 c.c.) $AlCl_3$ (anhydrous, 16 g.) was added and the mixture was heated slowly to 150°. The temperature was maintained at 150°-160° for 1½ hours. After cooling, the reaction mixture was poured into ice-cold dilute HCl. Removal of nitrobenzene by steam-distillation left a black mass. It was extracted with a 5% solution of NaOH and the extract acidified. The precipitate was again extracted with a saturated solution of sodium bicarbonate and the insoluble black residue was discarded. The sodium bicarbonate extract on acidifying furnished 3.95 g. of a mixture. Extraction of this with cold benzene and evaporation of benzene yielded 1.55 g. of 7-hydroxy-4-methyl-8-phenylsulphonylcoumarin which crystallised from ethanol or benzene in needles and melted at 220-21°.

The benzene-insoluble portion (2.4 g.) crystallised as rhombic plates from glacial acetic acid, m.p. 284-86° (with or without a synthetic sample of 7-hydroxy-4-methyl-6-phenylsulphonylcoumarin, *vide infra*). (Found : C, 60.6 ; H, 3.6. $C_{16}H_{12}O_5S$ requires C, 60.75 ; H, 3.8 per cent).

Both the isomers show bright blue fluorescence in ethanol, acetone and H_2SO_4 (conc.). They dissolve in alkali with intense violet fluorescence.

Alkaline Cleavage of 7-Hydroxy-4-methyl-8-phenylsulphonylcoumarin.—The coumarin (1.5 g.) was dissolved in 20% NaOH solution (240 c.c.) and refluxed for 7 hours. On acidifying the cooled solution with HCl, 2 : 6-*dihydroxydiphenylsulphone* (1.05 g.) was precipitated. It crystallised in needles from ethanol, m.p. 117-18°. There was no depression in melting point on admixture with a synthetic sample (*vide infra*). (Found : C, 57.9 ; H, 4.1. $C_{12}H_{10}O_4S$ requires C, 57.6 ; H, 4.0 per cent).

2 : 4-*Dimethoxydiphenyl Sulphide.*—Sodium (2.9 g.) was dissolved in absolute ethanol (30 c.c.) and to the resulting sodium ethoxide was added thiophenol (13.8 g.). The alcohol was then removed by evaporation. To the dry sodium thiophenate were

added 2 : 4-dimethoxyiodobenzene (33.1 g.) (Kauffmann and Kieser, *Ber.*, 1912, **45**, 2334) and copper powder (2 g.) and the mixture was heated in an oil-bath at 220°-230° for 2½ hours, using an air condenser. After cooling, the product was treated with H_2SO_4 (1 : 1; 50 c.c.) and zinc dust (10 g.) and subjected to steam-distillation. The residue was extracted with ether and dried ($CaCl_2$). On evaporation of the ether, an oily substance was obtained which solidified gradually. The yield was 29 g. Recrystallisation from ethanol afforded colorless needles, m.p. 63-64.5°. (Found: C, 68.4; H, 5.8. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7 per cent).

2 : 4-*Dimethoxydiphenylsulphone*.—The foregoing sulphide was dissolved in glacial acetic acid, excess of $KMnO_4$ solution (5%) was added and kept aside for 30 minutes and then decolorised with SO_2. The sulphone separated in quantitative yield. Recrystallisation from ethanol furnished colorless needles, m.p. 120-21°. Burton and Hoggarth (*J. Chem. Soc.*, 1945, 14), who prepared it from 2 : 4-dimethoxybenzene and benzenesulphonyl chloride by the Friedel-Crafts reaction, report m p. 121-22°.

2:4-*Dihydroxydiphenylsulphone*. —The above sulphone (3.3 g.), when demethylated with HI (*d* 1.7, 20 c.c.) at 200° for 3 hours, furnished 2:4-dihydroxydiphenylsulphone (2.15 g.). It crystallised from ethanol in rhombic plates, m.p. 128-29°. Burton and Hoggarth (*loc. cit.*) report m.p. 121-22°. Huismann (U.S.P. 2, 288, 282/1942) reports m.p. 115-16°, and later in another patent (D.R.P. 745,127/1943) reports m.p. 137-38°.

7-*Hydroxy*-4-*methyl*-6-*phenylsulphonylcoumarin* was obtained by the Pechmann condensation of 2:4-dihydroxydiphenylsulphone with ethyl acetoacetate. On recrystallising from glacial acetic acid, it melted at 284-86°. (Found: C, 61.1; H, 3.8. $C_{16}H_{10}O_5S$ requires C, 60.8; H, 3.8 per cent).

2 : 4-*Dimethoxy*-4′-*methyldiphenyl sulphide* was obtained in 92% yield by the same method as was used for 2:4-dimethoxydiphenyl sulphide, b.p. 250°/44 mm. (Found: C, 69 0; H, 6.1. $C_{15}H_{16}O_2S$ requires C, 69.2; H, 6.2 per cent).

2:4-*Dimethoxy*-4′-*methyldiphenylsulphone*.—Oxidation of the foregoing sulphide in glacial acetic acid with $KMnO_4$ yielded the *sulphone* in quantitative yield. The substance crystallised in colorless prisms from ethanol, m.p. 156-57°. (Found: C, 61.5; H, 6.0. $C_{15}H_{16}O_4S$ requires C, 61.7; H, 5.5 per cent).

2:4-*Dihydroxy*-4′-*methyldiphenylsulphone*.—Demethylation of the above sulphone with HI in the usual way furnished the 2:4-dihydroxy compound which crystallised from benzene in prisms, m.p. 155-56°. (Found: C, 55.4; H, 4.9. $C_{13}H_{12}O_4S.H_2O$ requires C, 55.3; H, 5.0 per cent).

It condensed with ethyl acetoacetate in the presence of H_2SO_4 (conc.) yielding 7-hydroxy-4-methyl-6-*p*-toluenesulphonylcoumarin, m.p. 250-52° (from ethanol) (cf. Bhavsar and Desai, *loc. cit.*).

2:6-*Dimethoxydiphenyl Sulphide*.—The method employed for its preparation was the same as that used for 2:4-dimethoxydiphenyl sulphide. 2:6-Dimethoxyiodobenzene required for the reaction was prepared by the method of Kauffmann and Franck (*Ber.*, 1907, **40**, 3999). The sulphide was obtained in 65% yield. The crude sulphide was highly coloured. Most of the colour was removed by treatment with animal charcoal

in boiling benzene. Final crystallisation from ethanol afforded colorless needles, m.p. 92-94°. (Found: C, 68.1 ; H, 5.5. $C_{14}H_{14}O_2S$ requires C, 68.3 ; H, 5.7 per cent).

2:6-*Dimethoxydiphenylsulphone*.—The foregoing sulphide (2.5 g.) was treated in glacial acetic acid with excess of $KMnO_4$ solution and left overnight. The solution was then decolorised with SO_2 and neutralised with ammonia. The precipitated *sulphone* was extracted with ether. Evaporation of the ether yielded 1.5 g. (54%) of the sulphone. Recrystallisation from ligroin gave fine needles, m.p. 126-27°. (Found : C, 59.9 ; H, 4.9. $C_{14}H_{14}O_4S$ requires C, 60.4 ; H, 5.0 per cent).

Demethylation of the above sulphone with HI yielded 89% of the 2:6-dihydroxy compound. It crystallised in fine needles from water and melted at 80-82°. After drying *in vacuo* the compound melted at 117-18°. (Found : C, 57.6 ; H, 4.2. Calc. for $C_{12}H_{10}O_4S$: C, 57.6; H, 4.0 per cent).

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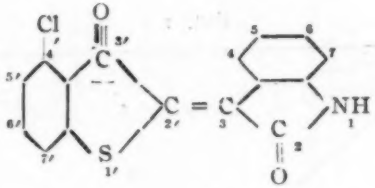
INDIGOID VAT DYES OF THE ISATIN SERIES. PART IX. 3-INDOLE-2′-(4′-CHLORO)THIONAPHTHENE-INDIGOS

By Sisir Kumar Guha, Jnanendra Nath Chatterjea and Arun Kumar Sinha

A few 3-indole-2′-(4′-chloro)thionaphthene-indigos have been prepared by the condensation of 4-chloro-3-hydroxythionaphthene with isatin and some of its important substituted products. These indigoid dyes are deeper in shade than those of the corresponding 6′-chloro compounds and lighter than those of the corresponding 5′-chloro and 7′-chloro products, studied earlier. The details of the preparation of 4-chloro-3-hydroxythionaphthene have been worked out

With a view to ascertaining the change in colour in relation to chemical constitution of the theoretically possible four isomeric 3-indole-2′-(chloro)thionaphthene-indigos, the influence of a chlorine atom in 5′-, 6′- and 7′-position of the thionaphthene ring of 3-indole-2′-thionaphthene-indigos (Thioindigo Scarlet R, Ciba Red G, etc.) was studied in Parts V, VI and VIII of this series (Guha and Basu-Mallick, this *Journal*, 1946, **23**, 211 ; Guha and Chatterjea, *ibid.*, 1947, **24**, 473 ; 1955, **32**, 551).

The chief object of the investigation has been achieved now by the preparation of 3-indole-2′-(4′-chloro)thionaphthene-indigos and thus completing the series. The dyes prepared are 3-indole-, 3-(5-chloro)indole-, 3-(5-bromo)indole-, 3-(5 : 7-dibromo)indole-, 3-(5-bromo-7-nitro)indole-, 3-(5 : 7-dinitro)indole-2′-(4′-chloro)thionaphthene-indigos, represented by the general formula (I).



(I)

The compounds of this class are well-crystalline darkish red, brownish red and violet-red substances, not melting below 310°. They are soluble in pyridine, nitrobenzene, aniline and dioxane. The parent dye, its bromonitro and the dinitro derivatives are soluble in xylene. All the substances are sparingly soluble in benzene, acetone, alcohol and more so in carbon tetrachloride. The bromonitro compound dissolves in cold strong sulphuric acid producing a blue solution and the rest of the compounds produce a violet solution when treated similarly. From an alkaline hydrosulphite vat at 60°-65°, the dyeing shades of the compounds were developed on cotton in beautiful uniform shade. The colour of the vat was similar to what was observed in case of 6′-chloro compounds (*loc. cit.*).

A comparison of the colour, dyed shades and absorption curves (Fig. 1) of some of the dyes of this 4′-chloro series with those of the corresponding substances of 5′-, 6′- and

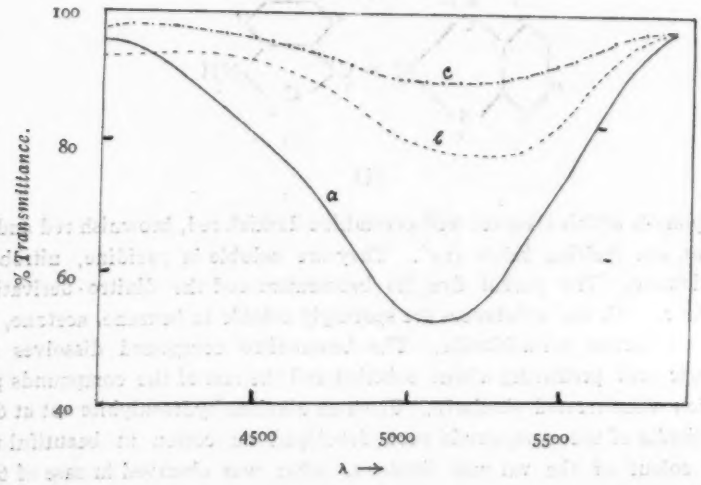
7′-chloro series (*loc. cit.*) reveals clearly that the change in colour of the four isomeric indole-(chloro)thionaphthene-indigos may be arranged in the following order: 5′-chloro dyes > 7′-chloro dyes > 4′-chloro dyes > 6′-chloro dyes. The position of the parent dyes, namely, 2-indole-, 3-(5:7-dibromo)indole- and 3-(5:7-dinitro)indole-2′-thionaphthene-indigos (Guha, this *Journal*, 1938, **15**, 501; 1939, **16**, 220; 1944, **21**, 89) is next to their 6′-chloro derivatives (Table I).

TABLE I

[T denotes thionaphthene-indigo]

Compound.	Dyed shade on cotton.	Absorption maxima.
3-Indole-2′-(5′-chloro)-T	Deep red	5150
3- ,, -2′-(7′-chloro)-T	Darkish red	5060
3- ,, -2′-(4′-chloro)-T	Deep red	5050
3- ,, -2′-(6′-chloro)-T	Light red (not fully developed)	5000
3-Indole-2′-T	Scarlet-red	4892
3-(5:7-Dibromo)-indole-2′-(5′-chloro)-T	Violet red	5200
3- ,, ,, -2′-(7′-chloro)-T	,,	5110
3- ,, ,, -2′-(4′ chloro)-T	,,	5100
3- ,, ,, -2′-(6′-chloro)-T	Deep red	5030
3- ,, ,, -2′-T	Yellowish red	4915
3-(5:7-Dinitro)-indole-2′-(5′-chloro)-T	Deep violet-red	5250
3- ,, ,, -2′-(7′-chloro)-T	Darkish violet red	5220
3- ,, ,, -2′-(4′-chloro)-T	,,	5200
3- ,, ,, -2′-(6′-chloro)-T	,,	5100
3- ,, ,, -2′-T	Dark red	4950

FIG. 1



a—3-Indole-2′-(4′-chloro)-T.
b—3-(5:7-dinitro)indole-2′-(4′-chloro)-T.
c—3-(5:7-dibromo) ,, ,, T.

4-1850-P.-12

TABLE II

[T = Thionaphthene-indigo; D = 4-chloro-5-hydroxythionaphthene].

Name	Mol. formula.	Constituents and glacial acetic acid used.	Appearance and yield.	Dyeing shade on cotton.	Solubility.	Analysis Found.	Analysis Calc.
3-Indole-2′-(4′-chloro)-T	$C_{16}H_8O_2NClS$	Isatin (0.29 g.) + D (0.37 g.); 30 c.c.	Bundles of darkish red long needles; 0.38 g. (60.4%)	Red	Difficultly in toluene	Cl, 11.5%	11.32%
3-(5-Chloro)indole-2′-(4′-chloro)-T	$C_{16}H_7O_2NCl_2S$	5-Chloroisatin (0.36 g.) + D (0.37 g.); 30 c.c.	Brownish red woolv crystalline mass; 0.59 g. (84.5%)	Deep Red	Moderately in toluene, difficultly in xylene	Cl, 20.7	20.4
3-(5-Bromo)indole-2′-(4′-chloro)-T	$C_{16}H_7O_2NClBrS$	5-Bromoisatin (0.45 g.) + D (0.37 g.); 35 c.c.	Long fibrous deep brownish red needles; 0.62 g. (78.7%)	Do	Difficultly in toluene and xylene	Cl, 9.2 Br, 20.4	9.0 20.4
3-(5:7-Dibromo)indole-2′-(4′-chloro)-T	$C_{16}H_6O_2NCl\,Br_2S$	5:7-Dibromoisatin (0.61 g.) + D (0.37 g.); 40 c.c.	Long sharp dark brownish red needles; 0.82 g. (86.7%)	Violet-red	Moderately in xylene; sparingly in toluene	Cl, 7.7 Br, 34.2	7.5 33.9
3-(5-Bromo-7-nitro)indole-2′-(4′-chloro)-T	$C_{16}H_6O_4N_2ClBrS$	5-Bromo-7-nitroisatin (0.41 g.) + D (0.28 g.); 30 c.c.	Shining violet-red plates; 0.55 g. (83.6%)	Brownish red	Moderately in toluene	Cl, 8.2 Br, 18.4	8.1 18.3
3-(5:7-Dinitro)indole-2′-(4′-chloro)-T	$C_{16}H_6O_6N_2ClS$	5:7-Dinitroisatin (0.47 g.) + D (0.37 g.); 40 c.c.	Violet-red small needles; 0.71 g. (87.7%)	Darkish violet-red	Do	Cl, 8.4	8.8
4:4′-Dichlorothioindigo	$C_{16}H_6O_2Cl_2S_2$	D (0.65 g.) in 40 c.c. NaOH soln. (10%) oxidised by K_3FeCy_6 soln. (5%)	Shining violet-red bundles of long needles; 0.54 g. (86.5%)	Violet-red	Difficultly in aniline; moderately in pyridine	Cl, 19.1	19.5

The starting material for the preparation of 4-chloro-3-hydroxythionaphthene is 6-chloro-2-nitrotoluene. The oxidation of this compound was carried out by potassium permanganate according to Green and Lawson (*J. Chem. Soc.*, 1891, **59**, 1013). The details, now worked out, have furnished consistently pure product and a high percentage of yield. It was found more convenient to use potassium permanganate in place of nitric acid used by Meyer (*Ber.*, 1895, **28**, 182). Next 6-chloro-2-nitrobenzoic acid was reduced to the corresponding amino compound with ferrous sulphate and ammonia (cf. Hunn, *J. Amer. Chem. Soc.*, 1923, **45**, 1024). Cohn (*Monatsh.*, 1901, **22**, 486) prepared the aminobenzoic acid by another route: 6-chloro-*o*-nitrotoluene → 6-chloro-*o*-toluidine → 6-chloro-*o*-acetotoluidide → 6-chloro-*o*-acetylaminobenzoic acid → 6-chloroanthranilic acid. The related hydrochloride was then converted through diazotisation, xanthogenation and condensation with monochloroacetic acid into 3-chlorophenylthioglycollic acid-2-carboxylic acid which on cyclisation furnished 4-chloro-3-hydroxythionaphthene (cf. F. P. 695, 763/1930; *Chem. Zentrl.*, 1931, **102**, II, 321). Dalgleish and Mann also prepared this compound by a long different route which the present authors did not find adoptable for this investigation (*J. Chem. Soc.*, 1945, 900).

The symmetrical dye, 4:4′-dichlorothioindigo (cf. F. P., *loc. cit.* Dalgleish and Mann, *loc. cit.*) was obtained by the oxidation of 4-chloro-3-hydroxythionaphthene in the usual way and crystallised from nitrobenzene, not melting below 310°. It is soluble in nitrobenzene, sparingly soluble in benzene, toluene, xylene, dioxane, carbon tetrachloride, acetone, and insoluble in alcohol. It dissolves in strong sulphuric acid producing a green solution. The alkaline hydrosulphite vat of the dye is deep yellow.

EXPERIMENTAL

6-Chloro-2-nitrobenzoic Acid.—6-Chloro-2-nitrotoluene (10 g.) was added to a solution of $KMnO_4$ (20 g.) in 1 litre of water and refluxed for 6 hours when the pink colour disappeared. The material was then cooled with ice and filtered and the residual unchanged product was recovered. The filtrate was concentrated on the water-bath, cooled and acidified. The precipitate was collected and crystallised from water in colorless needles, m. p. 161°, yield 10 g. (85%). Green and Lawson (*loc. cit.*) also record m. p. 161°.

6-Chloro-2-aminobenzoic Acid.—The foregoing acid (14 g.) was dissolved in aqueous ammonia (175 c.c., 15%) and to this solution ferrous sulphate (130 g.) in water (420 c.c.) was added. A dark brown precipitate was formed. The mixture was heated on the water-bath for 2 hours. To the cooled product an aqueous solution of NaOH (35 g. in 100 c. c.) was added, stirred well and filtered. The filtrate was acidified with strong HCl and allowed to stand for 4 to 5 hours when pinkish white precipitate of the hydrochloride of 6-chloroanthranilic acid separated (9.3 g.). It was crystallised from strong HCl in rectangular plates, m. p. 195° (Cohn, *loc. cit.*, records m.p. 195°). (Found: C, 40.1; H, 3.3. Calc. for $C_7H_7O_2NCl_2$: C, 40.4; H, 3.3 per cent).

4-Chloro-3-hydroxythionaphthene.—The above hydrochloride (5 g.) was dissolved in a solution of HCl (conc., 7.5 c. c.) in water (30 c. c.) and treated with a solution of sodium nitrite (1.75 g.) in water (18 c. c.) at 0°-5°. The diazo solution was then added

dropwise to a cooled solution of ethyl potassium xanthate (5 g.) in water (75 c. c.) containing sodium carbonate (10 g.). The mixture was allowed to attain room temperature (32°). The resulting xanthate was extracted with ether and the oily product was boiled under reflux with a mixture of sodium hydroxide (6.5 g.), water (10 c. c.) and alcohol (30 c. c.) for 5 hours. A solution of monochloroacetic acid (4.1 g.), neutralised with dilute sodium carbonate solution, was gradually added and the boiling continued for ½ hour more, cooled and acidified with HCl. The 3-chlorophenylthioglycollic acid-2-carboxylic acid was obtained as a brown oil which had very little tendency to crystallise. It was extracted with ether and the crude product was cyclised to 4-chloro-3-hydroxythionaphthene with NaOH (9 g.) at 170°-180° for ½ hour. The mass was lixiviated with water, cooled and acidified with HCl and distilled in a current of steam. The thioindoxyl was crystallised from petroleum ether in long colorless needles, m. p. 117-18.5° (F. P., *loc. cit.*, records m.p. 119-20°; Dalgleish and Mann, *loc. cit.*, record 116-18°). (Found: C, 51.9; H, 3.0. Calc. for C_8H_5OClS: C, 52.0; H, 2.7 per cent). The p-*nitrobenzylidene* derivative, prepared from molar quantities of the constituents in alcoholic solution in presence of a little HCl (conc.), separated from benzene in orange plates, m. p. 271-72°. (Found: N, 4.7. $C_{15}H_8O_3NClS$ requires N, 4.4 per cent).

3-Indole-2′-(4′-chloro)thionophthene-indigos, mentioned in Table II, were prepared in the usual manner by boiling for 20-30 minutes the glacial acetic acid solution of the equimolecular quantities of the reactants in presence of strong hydrochloric acid (2-3 c. c.) and finally crystallised from nitrobenzene.

One of the authors (S. K. G.) takes this opportunity of expressing his thanks due to Dr. Harold Heiftez of Messrs Heifetz and Company (U. S. A.) for a gift of 6-chloro-2-nitrotoluene required for this investigation.

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KINETICS OF CATION EXCHANGE REACTION IN SOLVENT OTHER THAN WATER. PART II. EFFECT OF WATER ON EXCHANGE OF COPPER ION ON AMBERLITE IRC-50

By R. P. Shukla and R. P. Bhatnagar

The exchange reaction between $CuCl_2$ and the resin Amberlite IRC-50 (vide this *Journal*, 1955, **32**, 39) has been studied by adding water to the reacting system. Results show that although order of the reaction remains the same after adding water, the velocity constant and the reaction rate go on increasing with the increasing volume of added water.

In the previous paper (this *Journal*, 1955, **32**, 39) it was shown that the exchange reaction between Cu^{2+} and Amberlite IRC-50 in non-aqueous solvents was a reversible second order reaction. The present work was undertaken to study the effect of adding water to the reacting system.

Experimental

To 50.0 c.c. of $CuCl_2$ solution in ethyl alcohol a known volume of double distilled ion-free water and 2.0 g. of the resin Amberlite IRC-50 (Rohm & Haas Co., Philadelphia) in hydrogen form were added and the exchange reaction carried out under thermostatic condition. Each time 5.0 c c. of the solution was taken out from the reaction mixture and the copper titrated iodimetrically. The solution was well stirred by means of a magnetic stirrer. Results are recorded below.

Table I

Volume of water added = 5 c.c.

t.	$a-x$	x.	$\ln\left[\frac{x(a-2x_0)+ax_e}{a\,x_e-x)}\right]$.	$k\times10^3$.
0.0 min.	10.30	...	...	...
5.0	10.15	0.15	0.05919	0.25551
10.0	10.05	0.25	0.10201	0.22019
25.0	9.75	0.55	0.24008	0.20727
30.0	9.65	0.65	0.28903	0.20145
45.0	9.35	0.95	0.46884	0.22541
Infinity	8.60	1.70 (x_e)	...	...

. Average: 0.22196

TABLE II

Volume of water added = 10 c.c.

t.	$a-x$.	x.	$\ln\left[\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right]$.	$k\times10^3$.
0.0 min.	9.45	...	...	...
5.0	8.45	1.0	0.44332	...
20.0	8.00	1.45	0.98041	0.65121
25.0	7.70	1.75	1.29241	0.68843
40.0	7.60	1.85	1.84945	0.61414
Infinity	7.55	1.90 (x_e)	...	...
				Average: 0.65136

TABLE III

Volume of water added = 20 c.c.

t	$a-x$.	x.	$\ln\left[\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right]$.	$k\times10^3$.
0.0 min.	6.30	...	...	...
5.0	5.85	0.45	0.16891	1.0772
10.0	5.55	0.75	0.30545	0.97414
14.0	5.30	1.00	0.44492	0.94597
20.0	5.20	1.10	0.51120	0.81517
30.0	4.90	1.40	0.77526	0.82415
Infinity	4.50	1.80 (x_e)	...	...
				Average : 0.92752

TABLE IV

Volume of water added = 40.0 c.c.

t.	$a-x$.	x.	$\ln\left[\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right]$.	$k\times10^3$.
0.0 min.	8.10	...	...	...
5.0	7.30	0.80	0.53455	1.3199
10.0	7.05	1.05	1.14707	1.4282
15.0	6.80	1.30	1.64673	1.3568
Infinity	6.75	1.35 (x_e)	...	...
				Average : 1.3683

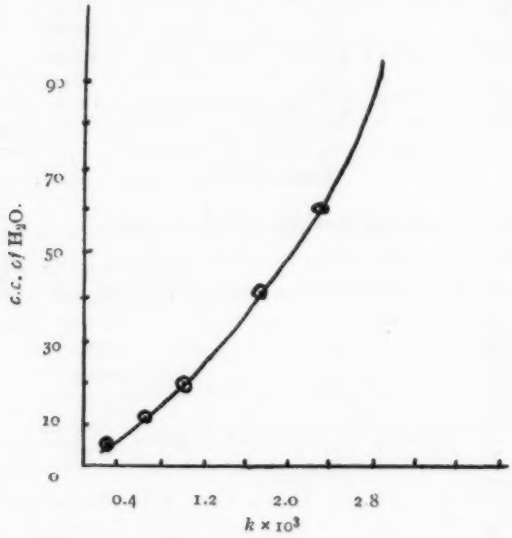
TABLE V

Volume of water added = 60 c.c.

t.	$a-x$.	x.	$\ln\left[\frac{x(a-2x_e)+ax_e}{a(x_e-x)}\right]$.	$k\times10^3$.
0.0 min.	5.26	...	...	...
5.0	4.70	0.55	0.75696	2.4030
7.0	4.65	0.60	0.89527	2.0300
10.0	4.55	0.70	1.39794	2.2190
Infinity	4.50	0.75 (x_e)	...	...
				Average : 2.217

As will be seen from the above tables, the order of the reaction remains the same even after adding water. However, the velocity constant and the reaction rate go on increasing as the volume of added water is increased. In the beginning, 'k' increases slowly but later on, rapidly, the rate of increase progressively decreases as can be seen from Fig. 1.

FIG. 1



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ANALYTICAL ASPECTS OF SOME ORGANIC COMPOUNDS. PART II. DETERMINATION OF PALLADIUM BY *p*-AMINOSALICYLIC ACID

By Sachindra Kumar Datta

Gravimetric and volumetric methods have been described for the determination of palladium with *p*-aminosalicylic acid. It produces a quantitative precipitation of a yellow complex of palladium at p_H 3.7. Separation of Pd may be carried out from a number of elements, including Pt, Au and vanadium. Fe, Ti, Zr and Th interfere; Ti, however, may be masked with sulphosalicylic acid. Volumetric method involves the use of bromide-bromate titration of the ligand.

The use of dimethylglyoxime in the separation and determination of palladium (Wunder and Thuringer, *Chem. Ztg.*, 1912, **36**, 550; *Z. anal. Chem.*, 1913, **52**, 101, 660, 740) has now practically superseded all other methods. A micro-method involving the use of methylbenzoylglyoxime (Holzer, *Z. anal. Chem.*, 1933, **95**, 392) has also proved fruitful.

p-Aminosalicylic acid was used by Datta and Banerjee (*Anal. Chim. Acta*, 1955, **13**, 23; this *Journal*, 1955, **32**, 687) for the determination of thorium and zirconium. During the investigation on the use of some phenolic acids as analytical reagents (Part I, *loc cit.*) it was noticed that *p*-aminosalicylic acid produced quantitative precipitation of palladium in weak acid medium. The application of this acid for the estimation of palladium, both gravimetrically and volumetrically, has been enumerated in the present communication. Palladium forms a yellow complex having the formula $Pd(C_7H_6O_3N)_2$ with P.A.S., which may be estimated by direct weighing or determined volumetrically by bromination of the ligand with potassium bromide-bromate, after decomposing the complex (Datta and Banerjee, *Anal. Chim. Acta*, 1955, **13**, 23). Separation of palladium from a number of common metals, like Cu, Ca, Ba, Sr, Co, Ni, etc., may also be carried out by using this reagent. Gold, platinum and vanadium also do not interfere, but metals, like Ti, Th, Zr and Fe interfere. Palladium, however, may be separated from titanium by masking the latter with sulphosalicylic acid.

Experimental

Reagent grade *p*-aminosalicylic acid was recrystallised from water and an 1% solution in water was prepared; on cooling this solution no crystals separated. A fresh solution of P.A.S. was prepared each day as the solution assumed a yellow colour on long standing. A 2% solution of P.A.S. in alcohol was also prepared for estimation. A.R. quality palladous chloride was dissolved with the aid of heat in the least quantity of HCl (conc.) and was then diluted with water to a definite volume. The palladium content was determined by the dimethylglyoxime method. Solutions of Ca, Ba, Sr, Al, Mg, Ti, U, Pt, V and Au were prepared from their nitrates, chlorides and sulphates, which were all of the reagent grade, and the metal contents were determined by standard methods.

Preparation and Composition of the Palladium Salt of P.A.S.

A solution of palladium chloride was diluted to 50 c.c. and warmed a little; to this was added dropwise with stirring an 1% solution of P.A.S. in cold water or a 2% solution of P.A.S. in alcohol, when a yellow precipitate appeared. The precipitate was allowed to stand for 1/2 hour and then filtered in a weighed sintered glass crucible, washed with warm water (40°) and then with hot alcohol several times and again with warm water till the filtrate did not produce any coloration with dilute $FeCl_3$ solution. The Pd salt was then dried in an electric oven at 110° for 4 hours to a constant weight.

In order to find out the composition, a weighed quantity of the Pd salt was ignited in a platinum crucible, first with a small flame, with special care that no vigorous evolution of fumes occurred which might carry off some amounts of the metal; the ignition was completed over a Meker burner. The residue was weighed as metal. The palladium content of the salt was also determined by decomposing a weighed amount of palladium salt with hot HCl (conc.). The solution was diluted with water and palladium was reprecipitated by an 1% HCl-dimethylglyoxime solution. The precipitate was filtered, washed, dried and weighed as $Pd(C_4H_7O_2N_2)_2$ in the usual manner. The nitrogen in the palladium salt of P.A.S. was also determined by the usual Kjeldahl method. The results recorded in Table I suggest the composition $Pd(C_7H_6O_3N)_2$ for the palladium salt of P.A.S. which requires Pd 22.2%. This may be represented as:

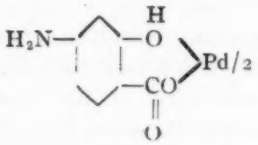

TABLE I

Analysis of palladium p-*aminosalicylate.*

A. By ingition method.

Pd salt dried at 110°.	Palladium: Found on ignition	Palladium: Calculated from salt.	N_2 in the dry salt: Found.	N_2 in the dry salt: Calc.
1. 0.0826 g.	0.0188 g.	0.0184 g.	0.0020 g.	0.0024 g.
2. 0.0531	0.0120	0.0118	0.0018	0.0015
3. 0.0408	0.0096	0.0091	0.0009	0.0012

B. By dimethylglyoxime method.

Pd salt of P.A.S. at 110°.	Pd salt of dimethylglyoxime.	Pd found in the salt of: P.A.S.	Dimethylglyoxime.
0.1021 g.	0.0701 g.	0.0227 g.	0.0222 g.
0.0867	0.0621	0.0192	0.0197
0.0501	0.0357	0.0111	0.0113

Precipitation Limit.—To the measured quantities of the solutions of palladium at 40°, diluted to a very great extent, a 2% alcoholic solution of P.A.S. was added. Distinct precipitates were visible up to 1 part of Pd in 100,000 parts of water; beyond this dilution only a slight opalescence was noticed.

Analytical Procedure.—An aliquot quantity of Pd solution was carefully neutralised to Congo red with 0.1*N*-NaOH, diluted to 40 c.c., and then warmed to 40°. To this solution was stirred in a 2% alcoholic solution of P.A.S. or an 1% cold solution of P.A.S. in water till the precipitation was complete (1 g. of P.A.S. per 0.2 g. of Pd). The mixture was kept at 40° for 15 minutes and then allowed to stand overnight. The precipitate was filtered, washed with warm water (40°) and then with hot alcohol in which the reagent was extremely soluble, and again with warm water. The precipitate was then dried at 110° to a constant weight. The amount of palladium was determined by multiplying that weight with the conversion factor 0.2224. As the Pd salt was sparingly soluble in hot water and in excess of the reagent, the precipitation was carried out by adding varied amounts of the reagent solution in water or alcohol, at different temperatures in order to find out the requisite amount necessary for the complete precipitation of a definite quantity of palladium. Some of the results are shown in Table II.

TABLE II

No.	Pd taken.	Reagent soln.	Temp.	Wt. of the Pd salt.	Pd calc.
1.	0.0168 g.	8 c.c. (alc. 2%)	40°	0.0755 g.	0.0168 g.
2.	0.0168	12 ,,	50°	0.0746	0.0166
3.	0.0168	15 ,,	70°	0.0710	0.0158
4.	0.0084	6 (aq. 1%)	40°	0 0387	0.0086
5.	,,	8 ,,	40°	0.0368	0.0082
6.	0.0084	10 (aq. 1%)	40°	0 0373	0 0083
7.	,,	15 ,,	40°	0.0359	0.0080
8.	,,	20 ,,	40°	0.0342	0.0076
9.	0.0126	15 ,,	50°	0.0553	0.0123
10.	,,	15 ,,	80°	0.0539	0.0120
11.	,,	15 ,,	100°	0.0 531	0.0118

It is seen from the above table that for the complete precipitation of palladium, about 10 c.c. of the reagent in aqueous solution (1%) or about 4 c.c. of the alcoholic solution (2%) could be safely added per 0.0084 g. of Pd, and the precipitation should be carried out between 40° and 50° as the palladium salt is slightly soluble at a higher temperature. At room temperature, however, the nature of the precipitate is not good. It was also noticed that better results were obtained with the alcoholic solution of the reagent than with its aqueous solution.

Precipitation at different p_H values.—In order to study the p_H ranges over which palladium could be completely precipitated by this reagent, estimation of palladium was carried out in solutions having different p_H values by following the same procedure as stated above. The precipitate was similarly filtered, washed and dried at 110° to a constant weight. The results, recorded in Table III, show that palladium is completely precipitated within a very narrow p_H range, namely, 3.7 to 4.2.

TABLE III

Pd taken = 0.0105 g.

p_H	1.8	2.0	2.4	3.0	3.5	3.7	4.0	4.2
Pd salt (g.)	0.0351	0.0373	0.0405	0.0455	0.0476	0.0472	0.0463	0.0454
Pdfoud (g.).	0.0078	0.0083	0.0090	0.0101	0.0106	0.0105	0.0103	0.0101
Error (mg.)	−2.7	−2.2	−1.5	−0.4	+0.1	±.0	−0.2	−0.4

Effect of Ammonium Ions.—It has been seen that the precipitation of Pd is retarded in the presence of ammonium ions. The Pd salt of P.A.S. is highly soluble in ammonium carbonate, ammonium thiocyanate, etc. The effect of ammonium ions was studied by adding various amounts of ammonium salts to the palladium solution. The results are recorded in Table IV.

TABLE IV

Pd taken.	Ammonium salts added.		Pd salt.	Pd found.	Error
0.0168 g.	NH_4Cl	0.5 g	0.0703 g.	0.0156 g.	−1.2 mg.
,,	,,	0.2	0.0721	0.0160	−0.8
,,	,,	0.1	0.0727	0.0162	−0.6
0.0105	NH_4OAc	0.2	0.0448	0.0099	−0.6
,,	,,	0.1	0.0456	0.0101	−0.4
0.0105	$(NH_4)_2CO_3$	0.5	0.0123	0.0027	−7.8
,,	,,	0.2	0.0230	0.0051	−5.4
0.0168	NH_4SCN	0.5	0.0508	0.0113	−5.5
,,	,,	0.2	0.0564	0.0125	−4.3
0.0168	NH_4NO_3	0.5	0.0711	0.0158	−1.0
,,	,,	0.2	0.0730	0.0163	−0.5

Estimation in presence of Foreign Ions.—Palladium can be estimated in presence of a large number of metal ions like, Cu, Al, Ba, Sr, Ca, Mg, Zn, Co and Ni etc., at p_H between 3.7 and 4 0 by following the same procedure. Palladium may also be separated from Pt, Au, U and vanadium. P.A.S. produces a grey turbidity with vanadium and reduces gold solution on boiling. But as the estimation of Pd is carried out below 45°, these metals do not interfere. Palladium may be separated from titanium by masking it with sulphosalicylic acid, the addition of the excess of which, however, retards the precipitation of palladium. The results are shown in Tables V and VI.

TABLE V

Palladium taken = 0.0212 g.

Metals taken.	Quantity.	Pd salt.	Pd found.	Error.
Copper	0.0423 g.	0.0914 g.	0.0210 g.	−0.2 mg.
Aluminium	0.0261	0.0957	0.0213	+0.1
Calcium	0.0531	0.0939	0.0209	−0.3
Barium	0.0223	0.0939	0.0209	−0.3
Strontium	0.0362	0.0946	0.0210	−0.2
Magnesium	0.0230	0.0962	0.0214	+0.2
Zinc	0.0152	0.0964	0.0214	+0.2
Nickel	0.0271	0.0976	0.0217	+0.5
Cobalt	0.0192	0.0971	0.0216	+0.4
Uranium	0.0314	0.0978	0.0217	+0.5
Platinum	0.0321	0.0966	0.0215	+0.3
Gold	0.0231	0.0973	0.0216	+0.4
Vanadium	0.0196	0.0977	0.0217	+0.5

TABLE VI

Palladium present = 0.0105 g.

Titanium added	Sulphosalicylic acid (5%).	Pd salt.	Pd found.	Error.
...	5 c.c.	0.0472 g.	0.0105 g.	±0.0 mg.
...	10	0.0453	0.0103	−0.2
0.0113 g.	10	0.0481	0.0107	+0.2
,,	12	0.0483	0.0107	+0.2
,,	15	0.0463	0.0103	−0.2
,,	20	0.0449	0.0100	−0.5
,,	23	0.0440	0.0098	−0.7
0.0226	20	0.0476	0.0106	+0.1
,,	30	0.0414	0.0092	−1.3

Volumetric Estimation of Palladium by P.A.S.

On decomposing the palladium salt of P.A.S, the ligand may be brominated by a standard bromide-bromate solution to furnish a dibrominated product (Gengrinovic and Baron, "Aptechoe Dele", 1952, pp. 27-30). The bromination method is based on the following reactions:

1. $Pd(C_7H_6O_3N)_2 + 2HCl \longrightarrow Pd^{2+} + 2Cl^- + 2C_7H_7O_3N$
2. $KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$
3. $2C_7H_7O_3N + 4Br_2 \longrightarrow 2C_7H_5O_3Br_2N + 4HBr$
4. $2KI + Br_2 \longrightarrow 2KBr + I_2$

From (1) and (3), it is evident that one atom of Pd^{II} is equivalent to 4 Br_2, and hence, its equivalent weight becomes Pd/8 or, 13.34. Therefore one atom of palladium is equivalent to 8 atoms of bromine, *i.e.*, 8000 c.c. of *N*-bromate. So, 1 c.c. of *N*-$KBrO_3 \equiv 0.01334$ g. of Pd.

Bromination Procedure.—The palladium salt of P.A.S. was precipitated from aliquot quantities of Pd solutions. The precipitate was filtered and washed as before in order to free it completely of the excess of the reagent ; the salt was dissolved in the least quantity of 0.1 *N*-NaOH, in which it was easily soluble; to it was then added 5 c.c. of HCl (1:1), boiled for 2 minutes and then cooled to room temperature ; the solution was diluted to 50 c.c. and was brominated by bromide-bromate mixture by the usual method (Datta and Banerjee, *loc.cit.*), the excess of bromine being determined iodimetrically. Some of the results of bromination are shown in Table VII.

TABLE VII

Palladium taken.	0.0683*N*-$KBrO_3$ used up.	Pd calc.	Diff.
0.0126 g.	14.1 c.c.	0 0128 g.	+0.2 mg.
0 0168	18.94	0.0172	+0.4
0.0189	21.5	0 0195	+0 6
0.0105	11.2	0.0102	−0.3
0.0095	9.9	0.0090	−0.5

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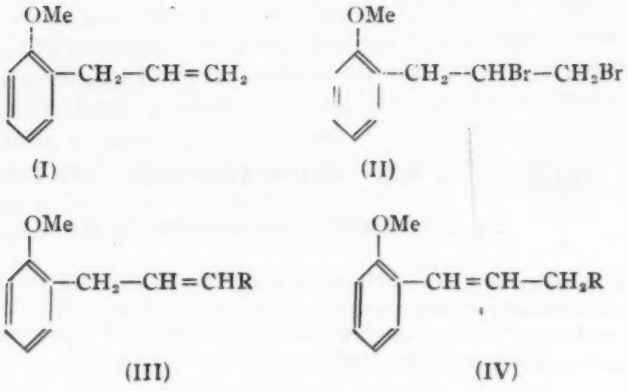
SEARCH FOR NEW ANTISPASMODICS. PART VII

By T. N. Ghosh and Saktipada Dutta

Interaction, even under mild condition, of 2:3-dibromo-1-(*o*-methoxyphenyl)propane (II) with diethylamine has furnished 1-(*o*-methoxyphenyl)-3-diethylamino-1-propene (IV). Condensation of ethyl cyanoacetate with either ω-acetamidobenzophenone or (α-acetamido-β-phenyl)-ethylmethyl ketone, in presence of ammonium acetate, has furnished a 3-pyrroline derivative.

Rodel and Bouteville (*Bull. soc. chim.*, 1949, 443) have synthesised esters of papaverine and *nor*-papaverine acids with diethylaminoethanol and have found them to possess appreciable antispasmodic property. It therefore appeared that *iso*-quinoline derivatives with side chains containing tertiary amino groups might be of importance in any attempt to correlate constitution with antispasmodic property. As an approach to the problem, *o*-methoxyallylbenzene (I) has been prepared and brominated to furnish 2:3-dibromo-1-(*o*-methoxyphenyl)propane (II). Clemo and Turnbull (*J. Chem. Soc.*, 1945, 533) have pointed to the low reactivity towards bases of the bromine atom in 2-position in compounds of the type (II). It was planned therefore to cause (II) to react under mild condition with a secondary amine, which would obviously attack the reactive bromine atom in the 3-position and then to treat the resulting base (a 2-bromo compound) with alcoholic ammonia under pressure. The final base, if obtained, would constitute a suitable starting material for the synthesis of *iso*quinolines of the type described above. Although the compound (II) readily undergoes reaction with diethylamine at room temperature in anhydrous ether, the base isolated is found to be an unsaturated compound having lost another molecule of hydrogen bromide and may be represented by either of the two formulations, (III) and (IV). In order to establish the structure, oxidation of the hydrochloride of the unsaturated compound was tried with periodic acid, but practically no oxidation took place under the conditions employed by Chatterjee and Ghosh (*J. Amer. Chem. Soc.*, 1954, **76**, 2459). However, Balbiano (*Ber.*, 1915, **48**, 394) has found that propenylphenols can be distinguished from allylphenols by their different behaviour towards mercuric acetate. The propenyl compounds are oxidised to glycols and mercurous acetate is precipitated, whereas the allyl compounds can add the elements of basic mercuric acetate, affording a solid addition product from which the allyl compound can be recovered by reduction with zinc and alkali. In the present case, treatment of the unsaturated compound with mercuric acetate in methanolic solution has yielded at room temperature a precipitate of mercurous acetate, uncontaminated with any trace of organic nitrogenous compound. This observation indicates that the compound under reference has the structure (IV). In view of the formation of the unsaturated compound (IV) in the above reaction, further work along this route has been abandoned.



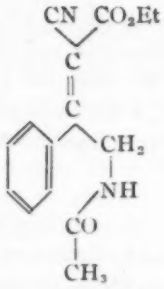
(I) (II)

(III) (IV)

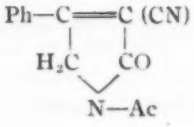
[R = diethylamino]

The second approach involves condensation of ω-acetamidobenzophenone with ethyl cyanoacetate in presence of ammonium acetate (cf. Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2327; Cope, Hofmann, Wyckoff and Hardenbergh, *ibid.*, 1941, **63**, 3452), so that ethyl α-cyano-β-phenyl-γ-acetamidocrotonate (V), if formed, could be catalytically hydrogenated and the corresponding propane subjected to the Bischler-Napieralski cyclisation. However, the compound isolated is found to be inert towards bromine and resistant towards catalytic hydrogenation. Moreover, it does not form any anilide when heated with aniline at 180° either alone or in presence of a trace of copper-bronze, indicating the absence of any carbethoxy group. These properties contra-indicate the structure (V), and it is apparent that (V), first formed, readily cyclises under the experimental condition to the 3-pyrroline derivative (VI), a structure which conforms to the analytical data and accords with the observations. On hydrolysis with 70% sulphuric acid the mono-acid (VII) is obtained. The possible alternative structure (VIII) (cf. McRae and Marion, *Canadian J. Res.*, 1937, **15B**, 480; Marion and McRae, *ibid.*, 1940, **18B**, 265; Cope, Hofmann, WycKoff and Hardenberg, *loc.cit.*) is excluded on the ground that the compound is devoid of any ketonic property and does not afford any semicarbazone or 2:4-dinitrophenylhydrazone. Further, the possibility of the intermediate (V) being a potentially tautomeric three-carbon system terminated by strongly negative groups at one end (cf. Birch, Kon and Norris, *J. Chem. Soc.*, 1923, **123**, 1361; Birch and Kon, *ibid.*, p. 2440) has been considered, so that (V) might tautomerise to (IX), which would then cyclise to (X). Whereas the compound isolated is not readily soluble in cold dilute alkali, a compound of the structure (X) should be acidic in nature because of the presence of the grouping, $CN.\overset{|}{C}H-CO-$, and should readily dissolve in alkali. The final outcome of these considerations leads to the conclusion that the compound under reference and its acid-hydrolysis product have the structures (VI) and (VII), respectively. With cold 10% caustic soda solution, (VI) is easily deacetylated to furnish (XI) which is readily soluble in cold dilute alkali and insoluble in aqueous sodium bicarbonate.

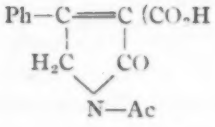
Similar condensation of ethyl cyanoacetate with (α-acetamido-β-phenyl)-ethylmethyl ketone in presence of ammonium acetate has furnished a compound behaving similarly as (VI), described above. On this basis, substantiated by analytical data, this condensation product has also been assigned the 3-pyrroline structure (XIII), formed *via* the intermediate compound (XII). Compound (XIII) is likewise easily deacetylated by cold 10% caustic soda solution to furnish (XIV).



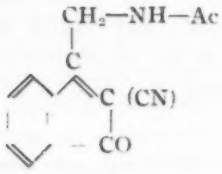
(V)



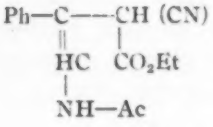
(VI)



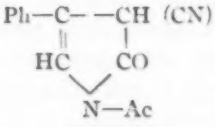
(VII)



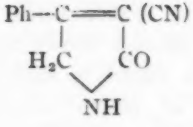
(VIII)



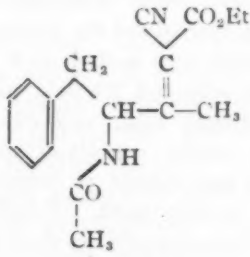
(IX)



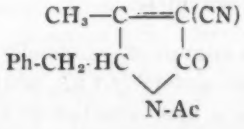
(X)



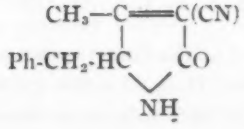
(XI)



(XII)



(XIII)



(XIV)

EXPERIMENTAL

o-Methoxyallylbenzene (I).—To a cooled solution of sodium (3.1 g.) in anhydrous methanol (60 c. c.) *o*-hydroxyallylbenzene (17 g.) was added and to the cooled mixture methyl iodide (20 g.) was added, all at a time. After allowing the mixture to stand for an hour it was heated on the water-bath under mild reflux for 12 hours, and every 2 hours methyl iodide (3 g.) was added. After distilling off the methanol the residue was treated with water and extracted with ether. The ethereal solution, after being washed with cold caustic soda solution (5%) and then with water, was dried over anhydrous sodium sulphate. Removal of the ether left a colorless liquid (15.2 g.), b. p. 98-100°/5-6 mm. (Found: C, 81.47; H, 8.34. $C_{10}H_{12}O$ requires C, 81.08 ; H, 8.11 per cent). It does not produce any distinctive coloration with ferric chloride.

2 : 3-*Dibromo* 1- (*o-methoxyphenyl*)*propane* (II).—To an ice-cooled solution of *o*-methoxyallylbenzene (25 g.) in anhydrous chloroform (30 c. c.) a solution of bromine (25 g.) in anhydrous chloroform (30 c. c.) was added dropwise under stirring during 1½ hours. After addition was over, stirring was continued for 2 hours more, when the solution turned almost colorless. The solution was poured into a mixture of ice and water and the chloroform layer after being washed thoroughly with water, then with caustic soda solution (5%) and finally with water, was dried over fused calcium chloride. Removal of the chloroform left a light brown heavy liquid (28 g.), b. p. 178-80°/6 mm. (Found : Br, 51.3. $C_{10}H_{12}OBr_2$ requires Br, 51.9 per cent).

1-(*o-Methoxyphenyl*)-3-*diethylamino*-1-*propene* (IV).—To an ice-cooled solution of the compound (II) (28 g.) in anhydrous ether (30 c.c.) a solution of diethylamine (35 g.) in anhydrous ether (30 c. c.) was added under stirring and the mixture was left in a closed vessel in a cool place. After 15 days diethylamine hydrobromide (14.5 g.) was filtered and the filtrate after removal of ether under suction furnished a liquid which was washed with water. The liquid was treated with cold, dilute hydrochloric acid and the acid solution, after being shaken thrice with ether, was just basified with cold, very dilute alkali. The reddish brown liquid (12 g.) was purified by similar acid-alkali treatment and was found to have a characteristic basic odour and devoid of bromine. It distilled at 167-70°/10 mm. to furnish a light yellow mobile liquid. (Found : N, 6.02. $C_{14}H_{21}ON$ requires N, 6.39 per cent). It readily decolorises bromine in chloroform solution.

The *picrate* was crystallised from ethanol in yellow needles, m. p. 110-12°. (Found : N, 12.3. $C_{14}H_{21}ON.C_6H_3O_7N_3$ requires N, 12.5 per cent).

1-*Acetyl*-2-*keto*-3-*cyano*-4-*phenyl*-3-*pyrroline* (VI).—A mixture of ω-acetamidobenzophenone (14 g.), ethyl cyanoacetate (10 g.), ammonium acetate (7.5 g.), acetic acid (30 c. c.) and anhydrous benzene (100 c.c.) was taken in a flask attached to a water separator (cf. Cope, Hofmann, Wyckoff and Hardenberg, *loc.cit.*), which in turn was

attached to a reflux condenser. The flask was heated at 140°-145° in an oil-bath for about 5 hours when water began to separate. Heating was continued till separation of water had ceased. The reaction mass was allowed to stand overnight when a crystalline solid separated. The solid was filtered, washed thoroughly with ether and crystallised twice from glacial acetic acid in fine brownish plates (8 g.), m. p. 214-16°. (Found : C, 68.89, 68.87 ; H, 4.52, 4.56 ; N, 12.07. $C_{13}H_{10}O_2N_2$ requires C, 69.02 ; H, 4.42 ; N, 12.38 per cent). It is not readily soluble in cold dilute alkali. It is insoluble in cold but soluble in warm concentrated hydrochloric acid; from the latter it crystallises on standing.

1-*Acetyl-2-keto-3-carboxy-4-phenyl-3-pyrroline* (VII).—A mixture of the above compound (VI, 4 g.) and 70% H_2SO_4 (40 c. c.) was refluxed on the wiregauze for about 8 hours. The liquid was decanted and the pasty solid thoroughly triturated with aqueous sodium bicarbonate solution. The alkaline solution was treated with Nuchar and filtered. The filtrate on acidification with HCl (conc.) furnished a solid which was twice crystallised from glacial acetic acid as a colorless, microcrystalline powder (2 g.), m. p. 236-38° with slight decomposition. (Found : C, 63.82 ; H, 4.42 ; N, 5.48. $C_{13}H_{11}O_4N$ requires C, 63.67 ; H, 4.49 ; N, 5.71 per cent). It is readily soluble in dilute ammonium hydroxide solution.

2-*Keto-3-cyano-4-phenyl-3-pyrroline* (XI).—The compound (VI, 4 g.) was triturated with caustic soda solution (10%, 120 c. c.) and the mixture briskly shaken at room temperature, when gradually most of the substance went into solution. The residue was similarly dissolved in another batch of caustic soda solution (10%, 50 c. c.). The combined alkaline solution was filtered and acidified under cooling with HCl (conc). The solid obtained was crystallised from ethanol in brownish slender needles (2 g.), melting at 210-11° to a dark viscous liquid (admixture with VI melts at 180-82°). (Found : N, 15.48 ; 15.52. $C_{11}H_8ON_2$ requires N, 15.21 per cent). It is insoluble in aqueous sodium bicarbonate but readily soluble in cold dilute alkali.

1-*Acetyl-2-keto-3-cyano-4-methyl-5-benzyl-3-pyrroline* (XIII).—The method of procedure was the same as described above. A mixture of (α-acetamido-β-phenyl)-ethylmethyl ketone (15 g.), ethyl cyanoacetate (10 g.), ammonium acetate (8 g.), anhydrous benzene (100 c. c.) and acetic acid (30 c. c.) was employed and the temperature of the oil-bath was maintained at 145°-150° for about 5 hours, when water began to separate. Heating was continued till no more water had separated. After distilling off the solvent, the residue was cooled, diluted with water and extracted with ether. The ethereal solution after being successively washed with cold sodium carbonate solution (5%) and water was dried over anhydrous sodium sulphate. Removal of the ether left a heavy liquid which solidified on scratching and trituration with ethanol. It was crystallised from aqueous ethanol in brownish needles (7 g.), m.p. 125-26°, and dried at 90°-95° *in vacuo* over P_2O_5. (Found : C, 70.48 ; H, 5.46 ; N, 10.8. $C_{15}H_{14}O_2N_2$ requires C, 70.86 ; H, 5.51 ; N, 11.02 per cent). It is inert towards bromine and resistant towards catalytic hydrogenation. It is insoluble in dilute mineral acids.

2-*Keto*-3-*cyano*-4-*methyl*-5-*benzyl*-3-*pyrroline* (XIV) was similarly prepared from (XIII) by treatment with 10% NaOH solution at room temperature. It was crystallised from ethanol as a colorless, microcrystalline powder, melting at 175-76° to a dark brown viscous liquid. (Found : N, 13.41. $C_{13}H_{12}ON_2$ requires N, 13.20 per cent). It is insoluble in aqueous sodium bicarbonate but readily soluble in cold dilute alkali.

The authors are grateful to Dr. U. P. Basu, Director of the Institute, for his interest.

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A NOTE ON 2-*p*-TOLYLIMINO 3-*p*-TOLYL-4-THIAZOLIDONE

By Prithwi Nath Bhargava and Bikkina Chitteyya

In continuation to the earlier work on 2-arylimino-3-aryl-4-thiazolidones (Bhargava, *J. Amer. Chem. Soc.*, 1951, **73**, 2353; Bhargava and Kaul, this *Journal*, 1955, **32**, 49), the present investigation has been extended to the preparation of 2-*p*-tolylimino-3-*p*-tolyl-4-thiazolidone, its condensation with ten aldehydes, one nitroso compound and two diazonium chlorides as well as to its oxidation to 2-*p*-tolylimino-3-*p*-tolyl-4-thiazolidone sulphone. Its hydrochloride has also been obtained. Reaction conditions on the formation of the thiazolidone have revealed that the highest yield (97.1%) is obtained when the amount of monochloroacetic acid is slightly in excess over the required molar quantity and the time of reflux is 8 hours. The secondary formation of 3-*p*-tolyl-2 : 4-thiazolidione has been successfully suppressed by the addition of a sufficient quantity of anhydrous sodium acetate, which removes HCl *in situ*.

2-p-*Tolylimino*-3-p-*tolyl*-4-*thiazolidone* was prepared according to the method of Klare, Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) in a yellow crystalline form, m.p. 127°. (Found : S, 10.90. $C_{17}H_{16}ON_2S$ requires S, 10.81 per cent).

2-p-*Tolylimino*-3-p-*tolyl*-5-*benzal*-4-*thiazolidone* was obtained by refluxing thiazolidone (1 g.), benzaldehyde (1.5 g.) and pyridine (6 c.c.) in a paraffin-bath at 150° for 7 hours. The residue was washed with HCl (dil.) and hot water, dried, and then dissolved in chloroform and reprecipitated by slow addition of alcohol.

Similarly other aldehydes and α-nitroso-β-naphthol were condensed yielding respectively 5-arylidene and 5-arylimino derivatives. The properties and analytical data of the different condensation products are recorded in Table I.

Table I

Nature of aldehydes or nitroso compound condensed.	Yield.	Colour.	M.P.	% Sulphur. Found.	Calc
Benzaldehyde	80%	Pale yellow	194°	8.52	8.33
Salicylaldehyde	75	Yellow	257°	7.82	8.00
Anisaldehyde	73	Pale yellow	210°	7.70	7.73
Cinnamaldehyde	70	Do	205°	7.76	7.80
o-Nitrobenzaldehyde	68	Yellow	143°	7.78	7.45
m- Do	70	Do	197°	7.42	7.45
p- Do	72	Pale yellow	233°	7.41	7.45
m-Hydroxybenzaldehyde	76	Brown	196°	7.39	7.40
Veratraldehyde	58	Yellow	199°	7.25	7.20
Piperonal	82	Brown	217°	7.45	7.47
α-Nitroso-β-naphthol	45	Black	225°	7.10	7.09

2-p-*Tolylimino*-3-p-*tolyl*-5-p-*toluneazo*-4-*thiazolidone*.—*p*-Toluidine (0.53 g.) in glacial acetic acid (50 c.c.) was diazotised with sodium nitrite (1.4 g.) and HCl (conc.,

10 c.c.) and to this a solution of the thiazolidone (1.2 g.) in acetic acid (30 c.c.) was slowly added at 0° while stirring. The mixture was poured on ice (300 g.) and the precipitate obtained was filtered, washed with water, dried and crystallised from alcohol.

Similarly condensation was effected with *p*-sulphonamidophenyldiazonium chloride. The properties of these compounds and their analytical data are recorded in Table II.

TABLE II

Diazonium chloride of amines.	Colour.	M.P.	% Sulphur. Found.	Calc.
p-Toluidine	Purple	192°	7.75	7.72
Sulphanilamide	Red	225°	13.30	13.37

2-p-*Tolylimino*-3-p-*tolyl*-4-*thiazolidone sulphone*, prepared according to the method of Pummerer (*Ber.*, 1910, **43**, 1407), was crystallised from alcohol in a yellow form, m.p. 145°. (Found : C, 62.1 ; H, 4.86 ; N, 8.45 ; S, 9.85. $C_{17}H_{16}O_3N_2S$ requires C, 62.19 ; H, 4.87 ; N, 8.53; S, 9.76 per cent).

2-p-*Tolylimino*-3-p-*tolyl*-4-*thiazolidone hydrochloride*, prepared as usual, was obtained in white crystalline form, m.p. 195°. (Found : C, 61.22; H, 5.14; N, 8.46; S, 9.58; HCl 10.92. $C_{17}H_{16}ON_2S.HCl$ requires C, 61.35; H, 5.11 ; N, 8.42; S, 9.62 ; HCl 10.97 per cent).

The authors are highly grateful to the authorities of the Banaras Hindu University for providing facilities in the Organic Chemical Laboratory. Thanks are also due to the U. P. Govt. Scientific Research Committee for the award of a special grant to one of them (P.N.B.).

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A NOTE ON GIBLING'S CORRECTIONS

By A. M. Talati

Gibling (*J. Chem. Soc.*, 1943, 149) assumed that since the interference corrections for C—C—C and C—C—O are 2.2 and 2.6 respectively, that for C—C—N should be 2.4. The author (this *Journal*, 1955, **32**, 471) has shown, however, that the interference corrections for C—C—C and C—C—O have the same value of 2.2. Hence, it is likely that the interference correction for C—C—N might also have the same value of 2.2.

The parachor value of $-NH_2$(aliph.) has been found to be 46.7 by Sugden, 44.0 by Vogel (*J. Chem. Soc.*, 1948, 1825) and 44.5 by Arbuzov and Guzhavina (*Doklady Akad. Nauk.*, 1948, **61**, 63). Gibling (*loc. cit.*) has calculated the parachor value of $(C)NH_2$ as 47.9 from the known parachor value of ammonia and not from the parachor value of organic amines. Bhagwat and Bakore (this *Journal*, 1948, **25**, 175) derived the group parachor value for the group (C) CH_2NH_2 as 83.4 as an average value from the values obtained for a series of compounds. In the present note the group parachor values for the groups $(C)CN_2NH_2$, $(C)_2CHNH_2$ and $(C)_3CNH_2$ have been derived from the parachor values of ethyl, *sec.*-butyl and *tert.*-amyl amines respectively.

The mean of the observed parachor values of ethylamine (Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1; Mumford and Philips, *J. Chem. Soc.*, 1929, 2112) may be taken as 139.7. From this the group parachor value for the group $(C)CH_2NH_2$ may be calculated as 84.3.

The group parachor value of methylamine (Jaeger, *loc. cit.*; Swift and Calkins, *J. Amer. Chem. Soc.*, 1943, **65**, 2416) may be taken as 99.7.

The group parachor value for the group $(C)_3CNH_2$ may be calculated as 46.9 from the parachor value of *tert.*-amylamine (Jaeger, and Mumford and Phillips, *loc. cit.*).

These values are recorded in Table I, together with those for groups $(C)CH_3$, $(C)_2CH_2$, $(C)_3CH$ and $(C)_4C$, as derived by Gibling (*J. Chem. Soc.*, 1941, 299).

Table I

Group or compound.	[*P*].	Diff.	Group.	[*P*].	Difference.
CH_3NH_2	99.7	...	$(C)CH_3$	55.2	...
$(C)CH_2NH_2$	84.3	15.4	$(C)_2CH_2$	39.8	15.4
$(C)_2CHNH_2$	66.7	17.6	$(C)_3CH$	22.2	17.6
$(C)_3CNH_2$	46.9	19.8	$(C)_4C$	2.4	19.8

The group parachor value for the group $(C)_2CHNH_2$ is suggested as 66.7 in Table I. The value of the group as found from the parachor value of *sec.*-butylamine observed by Vogel is 65.8, which is 0.9 lower than the suggested value.

It is seen from the results that the differences between the parachor values of the successive groups show a constant increment of 2.2 in both series. From these values the group parachor value for the group $(C)NH_2$ may be derived as 44.5 and the interference correction for C—C—N as 2.2, in the case of aliphatic primary amines if the parachor value of hydrogen is taken as 13.2, as derived by Gibling in the case of hydrocarbons (*J. Chem. Soc.*, 1945, 236). From these values, the ideal R.P. values for CH_3NH_2, $(C)CH_2NH_2$, $(C)_2CHNH_2$ and $(C)_3CNH_2$ may be calculated as 99.7, 86.5, 73.3 and 60.1 respectively. These results provide evidence in support of Gibling's assumption that the parachor value of the group $CH_3(N)$ is the same as the parachor value of the group $CH_3(C)$.

The author expresses his gratefulness to Dr. M. D. Avasare, for providing all facilities for the work and for taking interest in it.

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A NOTE ON THE CONDITIONS FOR OBTAINING CHROMATOGRAMS OF CATIONS ON ALUMINA FOR ESTIMATION FROM THE DIMENSIONS OF ZONE

By T. K. Meenakshisundaram and B. S. Srikantan

Chromatographic estimation of cations in solutions from the dimensions of the adsorptive zones on alumina column was attempted by Pinterovic (*Bull. Soc. Chim. Belg.*, 1949, **58**, 522), Srikantan and Krishnan (this *Journal*, 1949, **26**, 415), Schwab *et al.* (*Z. angrew. Chem.*, 1937, **50**, 546, 591 ; 1938, **51**, 709) and Srikantan and Venkatachalam, (this *Journal*, 1953, **30**, 167).

In order to make a quantitative determination of the cations from the dimension of the zone, it is necessary to specify the correct conditions for obtaining clear and uniform chromatograms. The following method of preparing a column of alumina was found to be very suitable for this purpose. The cation selected for estimation was Cu^{2+}. A 5% solution of potassium ferrocyanide was used for developing the chromatogram.

(*a*) *Alumina* .—Merck's standardised alumina (for chromatographic purposes) was sieved and particles passing through 200 mesh sieve were used. With this fine alumina the bands had no saw-edged ends. The alumina was boiled with 5 times its volume of water for 15 minutes and the hot slurry was subjected to powerful suction. This treatment helped in the removal of any air occluded in the alumina ; the resulting column was free from enclosed air bubbles. By repeated stirring with water and decantation the very fine particles were eliminated.

(*b*) *Preparation of the column for adsorption of the cations.*—Glass tubes (diameter 7 mm.) were attached to a wide reservoir of alumina slurrry at the top and ended in a jet at the bottom. The empty tube was fitted into a filter flask and the jet was plugged with cotton wool. The column was filled with water and the thick slurry was poured so that a column of 2 to 3 mm. was formed. It was tapped all round and a gentle suction applied. A uniform suction and a vigorous tapping helped to pack the tube tightly.

After packing to a height of 10 cm. the suction was continued and water was allowed to drain for 15 minutes. The suction was stopped and 10 c. c. of a buffer solution of p_H 9.5-10 (0.05 *M* borax solution) was allowed to drain without suction.

Adsorption on column.—A solution of Cu^{2+} [$CuSO_4$, $Cu(NO_3)_2$, $CuCl_2$] adjusted to p_H 5 was carefully poured so that it formed a layer just above the buffer solution which had almost completely passed into the column. It was then washed with 20-30 c. c. of the borax buffer solution, and then decolorised with the ferrocyanide solution. In view of the different p_H of the solutions used alternately on the column it was necessary to see that the solution did not interact on the top of the column. After development, the column was washed with water without causing diffusion of the bands.

About 80 to 90% of the columns, packed and worked in this way, furnished good bands enabling correct measurement of heights.

With standard solutions of copper sulphate, nitrate and chloride, estimations were done under similar conditions. It was found that, of the three cupric solutions, nitrate solution gave the longest band for the same amount of Cu^{2+}, a fact that recommended its use for a more accurate determination.

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REVIEWS

Einführung in die Ultraspektroskopie by Dr. Werner Brügel. Published by Dr. Dietrich Steinkopff, Darmstadt, 1954, pp. 366.

Infra-red spectroscopy has now become an indispensible tool for organic chemists and to some extent for biochemists. Its value to the inorganic chemists also has been amply demonstrated. A book on the theory and practice of infra-red spectroscopy, like the one under review, is therefore of much interest to research chemists.

Dr. Brügel's book seems to be the first one in German to deal exclusively with infra-red spectroscopy. It is divided into four sections. The first section presents a fairly detailed discussion of the theory of the infra-red spectra of substances in the gaseous state. The second section describes the different components of the infra-red spectrophotometers. The value of this section is enhanced by the information given in it about the commercially available equipments. The third section deals with the techniques of infra-red spectroscopy, both for qualitative and quantitative analysis. The last section consists of chapters on the characteristic absorption of the important functional groups, the calculated and observed spectra of a few simple molecules, infra-red spectra of high molecular substances and of inorganic compounds, and some special applications of infra-red spectroscopy. A long list of references to the published spectra of different types of organic compounds is also included in this section. This list will prove valuable although there are some important omissions.

To a practising organic chemist, the first section covering one quarter of the book will not be of as much use as the other sections. The value of the book would have been considerably enhanced if the first section were condensed and the chapter on the characteristic absorption of functional groups, which at present covers only twenty pages, were expanded. Scant attention has been paid to such an important topic as the detailed assignment of characteristic absorption for steroids by Norman Jones and co-workers. No mention has been made of the relationship between the spectra and conformation of functional groups.

The section describing methods of preparation of samples and other techniques of infra-red spectroscopy is up-to-date and well written. The book is illustrated with numerous diagrams and copies of spectra.

In spite of the shortcomings mentioned, the book under review would be an important addition to a chemistry library.

A.K.B.

Inorganic Chemistry by Fritz Ephraim. Revised by P. C. L. Thorne and E. R. Roberts. Sixth edition. Published by Oliver and Boyd, London, 1954. Pp.956 + xii. Price 35 sh. net.

Ephraim's Inorganic Chemistry revised by P. C. L. Thorne has always been a reference book to every student of Chemistry. Its instructive and novel approach, the

type of systematisation and grouping in classes of elements and compounds are seldom found in any other treatise of the type. In this sixth edition the same system, characteristics of earlier editions, has been maintained with minor changes and necessary additions.

In the chapter on structure of matter, a few lines have been devoted on electron levels, structure of nucleus, structure of molecules and electron diffraction.

The section on radioactivity and isotopes has been much revised with the incorporation of artificial radioactivity together with a short summary of the chemistry of transuranic and new radioactive elements, but no mention has been made regarding the work of Seaborg and Haissinsky over the controversial grouping of elements as actinons. An account of rare earths with a brief chemistry of hafnium, particularly with regard to its separation from zirconium, has been well written.

Pauling's theory of valency, the quanticule theory of Fajans and the molecular orbitals appear to have been written in most unhappy way and it is difficult for a reader to make a correct appraisal to their quality.

There are some noticeable misprints (liquid instead of ligand-p. 293 ;

$$[Cr^{Py_2}_{(H_2O)_4}]X \text{ instead of } [Cr^{Py_2}_{(H_2O)_4}]X_3\text{-p.334)},$$

mistreading of literature (inclusion of Pb in the stability order-p. 293) and similar other ambiguities which the revisers should rectify in their subsequent edition.

This Inorganic Chemistry of the descriptive type provides the reader with vast informations on the subject and every student of chemistry should have a copy of this reference book.

A.K.M.

Methoden der Organischen Chemie (houben-Weyl). Vol. IV. Allgemeine Chemiosha Methoden. Part II. Fourth edition. Edited by Eugen Müller. 1955, pp. 1004 + xxviii. Published by Georg Theime Verlag, Stuttgart, Germany.

The third edition of this outstanding treatise was published some twenty years ago. The recent rapid progress in experimental technique has necessitated a thorough revision and expansion of the earlier edition. The fourth edition of this encyclopaedic work is expected to cover 16 volumes. The prominent features of this edition are : (1) the sections have been compiled by competent authorities who have long practical experience in the particular field and hence these are authoritative and complete, (2) the subjects have been treated from the standpoint of practical methods suitable for preparative purposes. Consequently no undue prominence has been given to the theoretical treatment. The object of the book is to emphasise the different aspects of experimental procedures, and a careful perusal leaves one with the impression that this object has been admirably achieved.

The volume under review is organised into eleven sections, namely, 1. Acid-base catalysis, 2. Catalysis involving complex cations and anions, 3. Methods of production of catalysts and mixed catalysts, 4. Carrying out of heterogeneous catalytic reactions, 5. General methods for performing pyrochemical reactions, 6. Electrochemical reactions, 7. Methods of preparing optically active and inactive compounds, 8. Preparation of organic compounds containing isotopes, 9. Methods of production and transformation of large ring-system, 10. General methods for performing biochemical reactions and 11. Methods for performing microbiological-chemical reactions.

The book reflects considerable labour and traditional German thoroughness and precision. It embodies a mass of useful information which is to be most rewarding to research workers. The proper way to do something means saving oneself of much trouble and grief in the long run, and it must be said without any reserve that the book shows the right way to do it. Along with the text are given numerous illustrations of apparatus set-ups and designs, and diagrams. The book is attractively printed and well indexed, and covers literature and patents up to at least 1953. The series of "Methoden der Organischen Chemie" should be on the shelves of the library of every institute where research in, or advanced teaching of, organic chemistry is conducted.

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Errata

Page.	*Line.*	*Read.*	*For.*
49	8	diphenylthiourea	diphenylthioure
98	Table I, oclumn 7, line 1	$C_{16}H_{13}O_5N$	$C_6H_{13}O_5N$
99	Table III, column 6, last line	$C_{17}H_{13}O_6N$	$C_{17}H_{13}ON$
100	Table IV, column 5, line 7	264-65°	254-65°
119	Table I (contd.) column 5, last line	H, 5.1	H, 51
	Do column 6, last but 1 line	C, 71.1	C, 171.1
248	31	2 Hg_2BeF_3 OH, Hg_2O, 2 H_2O	$HgBeF_3$ OH, Hg_2O, H_2O
		(Table III-IV)	(Table I-II)
652	9	Table III	Table I
652	9	*thioammeline*	*thioammeiine*
653	Table II, title	Pd^{2+}	Pb^{2+}
653	Table II, last line	ω-acetamido-acetophenone	ω-acetamido-benzophenone
791	3 (abstract)		
792	1		
794	4 (from bottom)		

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